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<p>(21) International Application Number: PCT/US97/16705</p> <p>(22) International Filing Date: 22 September 1997 (22.09.97)</p> <p>(30) Priority Data: 9619928.6 24 September 1996 (24.09.96) GB 9713946.3 2 July 1997 (02.07.97) GB</p> <p>(71) Applicant (for all designated States except US): THE PROCTER &amp; GAMBLE COMPANY [US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): CALDARELLI, Jennifer, Leupoin [CA/GB]; 9797 Fawncreek Drive, Cincinnati, OH 45249 (US). ASKEW, Stuart, Clive [GB/GB]; 17 Mayfair Road, West Jesmond, Newcastle-upon-Tyne NE2 3DN (GB). SORRIE, Graham, Alexander [GB/GB]; 14 Curlew Hill, Morpeth, Northumberland NE61 3SH (GB). HALL, Robin, Gibson [GB/GB]; 27 Blackfriars Court, Stowell Street, Newcastle-upon-Tyne NE1 4XB (GB). HENSMAN, Tiffany, Alice [GB/GB]; 44 Deneside Court, Selbourn Gardens, Jesmond, Newcastle-upon-Tyne NE2 1JW (GB). TANTAWY, Hossam [GB/GB]; Woodend, Fawdon Walk, Kingston Park, Newcastle-upon-Tyne NE13 7AW (GB).</p>	<p>(74) Agents: REED, T., David et al.; The Procter &amp; Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p> <p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: DETERGENT COMPOSITION OR COMPONENT</p> <p>(57) Abstract</p> <p>The present invention relates to <u>solid</u> or ganular detergent composition or component or spray-dried particle containing one or more carboxylate-containing polyelectrolyte compounds, having builder or dispersant properties, and one or more cationic compounds, which are cationic, (partially) quaternized ethoxylated (poly)amine compounds with clay-soil removal/anti-redeposition properties, for use in laundry and dish washing processes.</p>		

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### **Detergent Composition or Component**

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### **Technical Field**

The present invention relates to a detergent composition or component containing  
15 cationic compounds with clay-soil/ particulate soil removal/anti-redeposition  
properties and one or more carboxylate-containing polyelectrolyte compounds,  
with builder or dispersant properties, for use in laundry and dish washing  
processes.

20

### **Background to the Invention**

A particularly important property of a detergent composition is its ability to  
remove particulate type soils from a variety of fabrics during laundering. One  
important particulate group of soils is the clay-type soils. Clay soil particles  
25 generally comprise negatively charged layers of aluminosilicates and positively  
charged cations (e.g. calcium) which are positioned between and hold together the  
negatively charged layers.

A variety of models can be proposed for compounds which have clay soil removal  
30 properties. One model requires that the compound have two distinct characteristics.  
The first is the ability of the compound to adsorb onto the negatively charged  
layers of the clay particle; and the ability of the compound, once adsorbed, to push  
apart (swell) the negatively charged layers so that the clay particle loses its  
cohesive force and can be removed in the wash water.

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In addition to clay soil removal, there is a need to keep the removed soil in suspension during the laundering (or dish washing) cycle. Soil which is removed from the fabric and suspended in the wash water can redeposit on the surface of the fabric. This redeposited soil causes a dulling or "greying" effect which is especially noticeable on white fabrics. To minimise this problem, anti-redeposition agents are also often included in detergent compositions.

Other detergent compounds traditionally employed in detergents are soil dispersants and anti-encrustation agent, such as carboxylate-containing polyelectrolyte compounds.

EP-B-111 965 discloses the use in detergents of cationic compounds, which have both clay-soil removal and anti-redeposition properties.

US 4,659,802 and US 4,664,848 describe quaternized amines which have clay-soil removal and anti-redeposition properties and which can be used in combination with anionic surfactants.

A model proposed for the anti-redeposition action of these compounds is as follows. Adsorption of the positively charged molecule on the surface of clay particles in the wash water gives the clay particles the dispersancy properties of the molecule. As more and more of these compounds adsorb onto the suspended clay soil particles, the latter become encased within a hydrophilic layer. As such the hydrophilically encased soil is prevented from redepositing on hydrophobic fabrics such as polyester, during the laundering or dish washing cycle.

It has been found that the known cationic clay-soil removal compounds do not always remove the clay particles rapidly and efficiently from the fabric surface into the washing water. This may be due to clay and particulate soils being held together by calcium bridges which may prevent the cationic clay soil removal compound from pushing apart the negatively charged layers of the clay, thereby preventing the clay particles losing their cohesive force.

It has also been found that the anti-redeposition properties of these known cationic clay-soil removal compounds can be diminished under hard-water conditions during the laundry or dishwashing process, i.e when a high level of free calcium (and/ or magnesium) is present in the wash water.

The Applicants have now found that these problems can be ameliorated by inclusion of specific amounts of carboxylate-containing polyelectrolyte compounds, which have builder or dispersant properties, in a detergent component or in a  
5 detergent composition comprising specific amounts of cationic, (partially) quaternized ethoxylated (poly) amines which have clay-soil removal/anti-redeposition properties. An example of such a component is a spray-dried granular particle. Such detergent components or detergent compositions have now been found to deliver a surprisingly better clay/ soil removal and cleaning performance  
10 than that of detergent compositions employing either of the two components individually. It has also been found that specific ratios of the cationic quaternized ethoxylated (poly) amines to the carboxylate-containing polyelectrolyte compounds are particularly preferred and enable good performance benefits to be achieved even when using very low amounts of each component.

15 The cleaning performance benefits of the detergent compositions containing both carboxylate-containing polyelectrolyte compounds and cationic, (partially) quaternized ethoxylated (poly) amines are found to depend both on the amount of carboxylate-containing polyelectrolyte compound used and its properties (e.g. the  
20 molecular weight of the polymeric compound and the monomeric segments comprised in the polymeric compound). For example, in built conditions it has been found that co-polymeric polycarboxylic compounds, for example maleic/ acrylic co-polymers, have a better (calcium) builder/ dispersant performance than homo-polymeric polycarboxylic compounds of a similar molecular weight. Thus,  
25 lower levels of certain, preferred polymeric compounds are as effective as higher levels of others.

A further advantage of the present invention is that the clay/ soil removal benefits can even be observed after the completion of only one wash cycle.

30 All documents cited in the present description are, in relevant part, incorporated herein by reference.

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Summary of the invention

5 In accordance with the present invention there is provided a solid, preferably a granular detergent composition or component thereof which comprises:

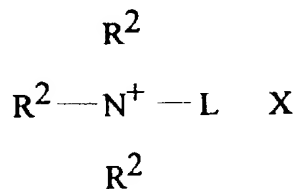
(a) a carboxylate-containing polyelectrolyte compound;  
and

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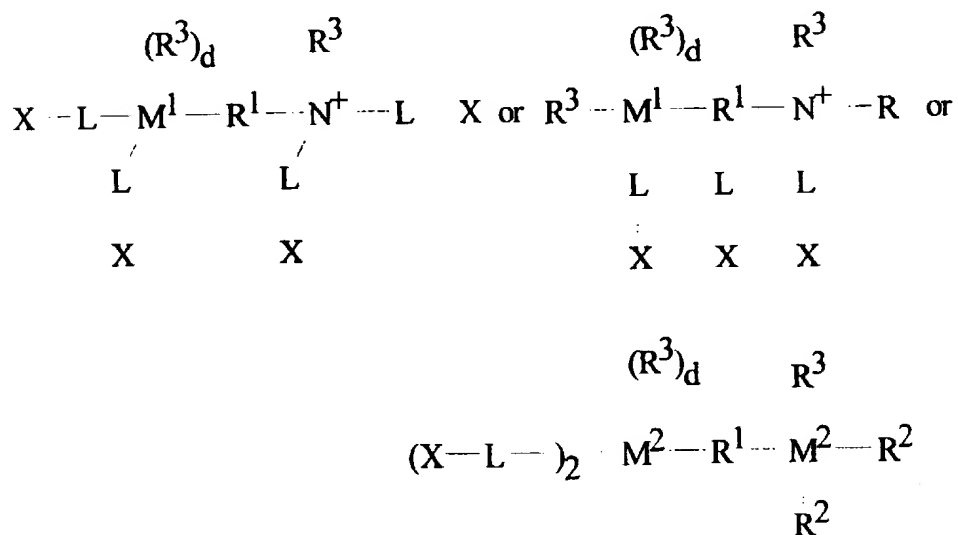
(b) a water-soluble cationic compound having clay soil removal/anti-redeposition properties, which is selected from the group consisting of:

1) ethoxylated cationic monoamines having the formula:

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2) ethoxylated cationic diamines having the formula:

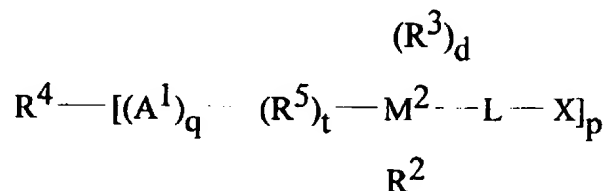


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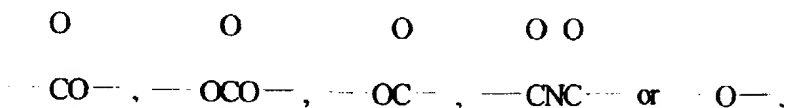
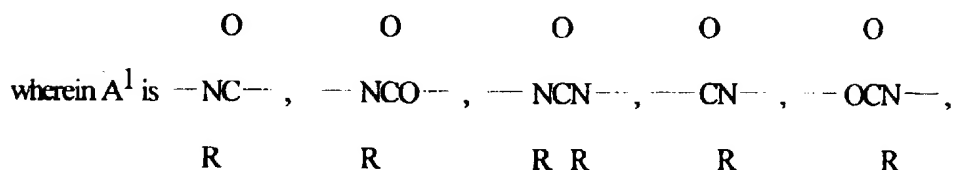
wherein  $M^1$  is an  $N^+$  or  $N$  group; each  $M^2$  is an  $N^+$  or  $N$  group, and at least one  $M^2$  is an  $N^+$  group;

3) ethoxylated cationic polyamines having the formula:

5



4) mixtures thereof;



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R

R is H or  $C_1$ - $C_4$  alkyl or hydroxyalkyl,  $R^1$  is  $C_2$ - $C_{12}$  alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a  $C_2$ - $C_3$  oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each  $R^2$  is  $C_1$ - $C_4$  alkyl or hydroxyalkyl, the moiety -L-X, or two  $R^2$  together form the moiety  $-(CH_2)_r-A^2-(CH_2)_s-$ , wherein  $A^2$  is -O- or  $-CH_2-$ , r is 1 or 2, s is 1 or 2 and r + s is 3 or 4; each  $R^3$  is  $C_1$ - $C_8$  alkyl or hydroxyalkyl, benzyl, the moiety L-X, or two  $R^3$  or one  $R^2$  and one  $R^3$  together form the moiety  $-(CH_2)_r-A^2-(CH_2)_s-$ ;  $R^4$  is a substituted  $C_3$ - $C_{12}$  alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl group having p substitution sites;  $R^5$  is  $C_1$ - $C_{12}$  alkenyl, hydroxyalkylene, alkenylene, arylene or alkarylene, or a  $C_2$ - $C_3$  oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; X is a nonionic group selected from the group consisting of H,  $C_1$ - $C_4$  alkyl or

20

hydroxyalkyl ester or ether groups, and mixtures thereof; L is a hydrophilic chain which contains the polyoxyalkylene moiety

$-(R^6O)_m(CH_2CH_2O)_n-$ ; wherein  $R^6$  is  $C_3$ - $C_4$  alkylene or hydroxyalkylene and m and n are numbers such that the moiety

- 5  $-(CH_2CH_2O)_n-$  comprises at least about 50% by weight of said polyoxyalkylene moiety; d is 1 when  $M^2$  is  $N^+$  and is 0 when  $M^2$  is N; n is at least about 16 for said cationic monoamines, is at least about 6 for said cationic diamines and is at least about 3 for said cationic polyamines; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1;

10

and wherein the ratio of (a) to (b) is from 1:95 to 95:1.

A preferred ratio of (a) to (b) is from 1:1 to 1:6.

- 15 Furthermore, it has been found that the detergent compositions but particularly the detergent components and especially the spray-dried particles comprising the cationic quaternized ethoxylated (poly) amines and the carboxylate-containing polyelectrolyte compounds in the specific levels and ratios are crisp and free flowing and do not have the tendency to cake, and are capable of absorbing other  
20 detergent compounds when present, such as for example anionic, cationic and nonionic surfactants. This thus minimises caking of the compositions comprising the components or spray-dried particles.

- Therefore in accordance with a preferred aspect of the invention is a spray-dried  
25 particle or granule comprising compounds (a) and (b) as described above and with (a) and (b) in a referred ratio of from 1:1 to 1:10.

Preferred anionic counterions for the cationic water-soluble compounds are halides such as  $Cl^-$  and  $Br^-$ , or most preferably  $MeSO_4^-$ .

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Detailed description of the invention

An essential feature of the present invention is a water-soluble cationic compound which has particulate soil/ clay-soil removal/anti-redeposition properties and which is selected from the group consisting of cationic mono-di- and polyamines.

The ratio in the composition or component thereof of the cationic compound to the carboxylate-containing polyelectrolyte compound is from 1:95 to 95:1, more preferably from 1:25 to 25:1, most preferably from 1:5 to 5:1.

Where low amounts of cationic compound and carboxylate-containing polyelectrolyte are used it may be preferred that the ratio of the carboxylate-containing polyelectrolyte compound to the water-soluble cationic compound in the component is preferably from 1:1 to 1:10, more preferably from 1:1 to 1:4, most preferably from 1:1 to 1:2.

If present in a detergent composition in accordance with the present invention the water-soluble cationic compound is preferably present at a level of from 0.01 % to 30%, more preferably from 0.1 % to 15% , most preferably from 0.2 % to 3.0 % by weight of the detergent composition.

In the spray-dried particle it is particularly preferred that the ratio of the carboxylate-containing polyelectrolyte compound to the water-soluble cationic compound in the component is from 1:1 to 1:10, more preferably from 1:1 to 1:4, most preferably from 1:1 to 1:2.

In the spray-dried particle or in a detergent component in accordance with the present invention the water-soluble cationic compound is preferably present at a level of from 0.1 % to 30%, more preferably from 0.5 % to 15% , even more preferably from 0.5 % to 7%, most preferably from 0.6 % to 2 % by weight of the spray-dried particle or detergent component.

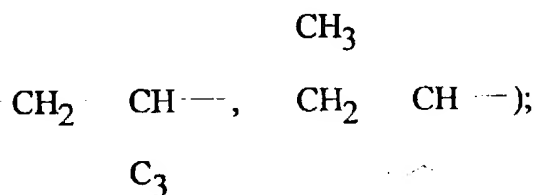
Such a spray-dried particle or such a component preferably is present in a granular detergent composition at a level of from 5 % to 90%, more preferably from 20 % to 60%, most preferably from 30 % to 50 % by weight of the composition.

Cationic amines

The water-soluble cationic compounds of the present invention useful in the detergent compositions or components in accord with the present invention include  
 5 ethoxylated cationic monoamines, ethoxylated cationic diamines and ethoxylated cationic polyamines as previously defined.

In the preceding formulas for the cationic amines, R<sup>1</sup> can be branched

10 (e.g.



cyclic (e.g. ) ,

or most preferably linear

15

(e.g.  $-\text{CH}_2\text{CH}_2-$  ,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$  )

alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene. R<sup>1</sup> is preferably C<sub>2</sub>-C<sub>6</sub> alkylene for the ethoxylated cationic diamines. Each R<sup>2</sup> is  
 20 preferably methyl or the moiety -L-X; each R<sup>3</sup> is preferably C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl, and most preferably methyl.

The positive charge of the N<sup>+</sup> groups is offset by the appropriate number of counter anions. Suitable counter anions include Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>3</sub><sup>-2</sup>, PO<sub>4</sub><sup>-2</sup>, MeSO<sub>4</sub><sup>-</sup>  
 25 and the like. Particularly preferred counter anions are Cl<sup>-</sup> and Br<sup>-</sup>, but most preferably MeSO<sub>4</sub><sup>-</sup>.

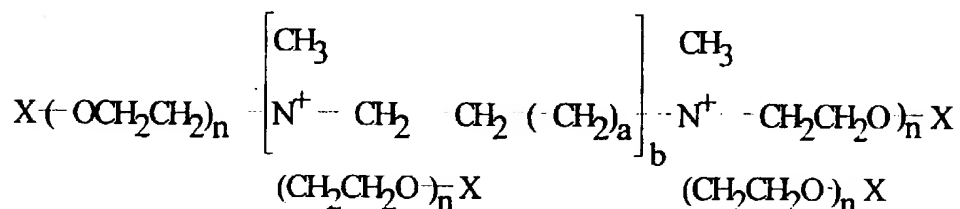
X can be a non-ionic group selected from hydrogen (H), C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl ester or ether groups, or mixtures thereof. Preferred esters or ethers are the acetate ester and methyl ether, respectively. The particularly preferred nonionic groups are H and the methyl ether.

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In the preceding formulas, hydrophilic chain L usually consists entirely of the polyoxyalkylene moiety  $-(R^6O)_m(CH_2CH_2O)_n-$ . The moieties  $-(R^6O)_m-$  and  $-(CH_2CH_2O)_n-$  of the polyoxyalkylene moiety can be mixed together or preferably form blocks of  $-(R^6O)_m-$  and  $-(CH_2CH_2O)_n-$  moieties. R<sup>6</sup> is preferably C<sub>3</sub>H<sub>6</sub> (propylene); m is preferably from 0 to about 5 and is most preferably 0, i.e. the polyoxyalkylene moiety consists entirely of the moiety  $-(CH_2CH_2O)_n-$ . The moiety  $-(CH_2CH_2O)_n-$  preferably comprises at least about 85% by weight of the polyoxyalkylene moiety and most preferably 100% by weight (m is 0).

15 In the preceding formulas, M<sup>1</sup> and each M<sup>2</sup> are preferably an N<sup>+</sup> group for the cationic diamines and polyamines.

Preferred ethoxylated cationic monoamines and diamines have the formula:



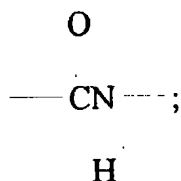
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wherein X and n are defined as before, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene), b is 1 or 0. For preferred cationic monoamines (b=0), n is preferably at least about 16, with a typical range of from about 20 to about 35. For preferred cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

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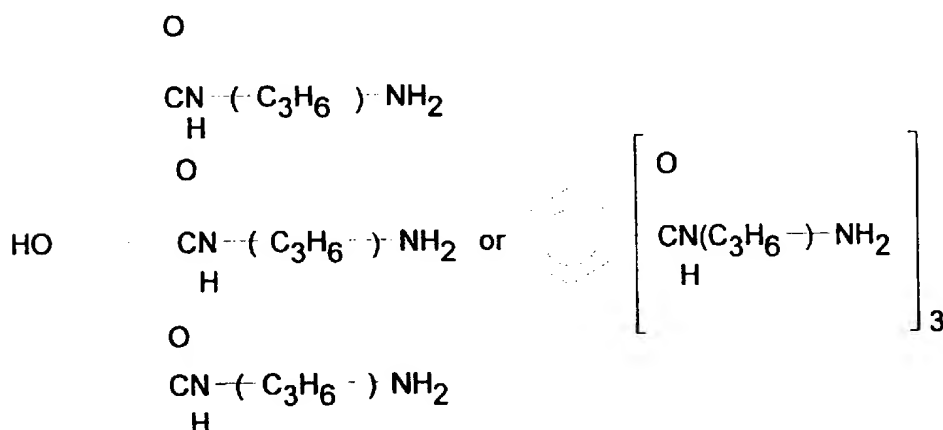
In the preceding formula for the ethoxylated cationic polyamines, R<sub>4</sub> (linear, branched, or cyclic) is preferably a substituted C<sub>3</sub>-C<sub>6</sub> alkyl, hydroxyalkyl or aryl group; A<sup>1</sup> is preferably

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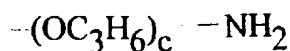
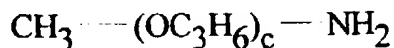
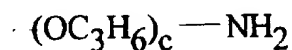


n is preferably at least about 12, with a typical range of from about 12 to about 42; p is preferably from 3 to 6. When R<sup>4</sup> is a substituted aryl or alkaryl group, q is preferably 1 and R<sup>5</sup> is preferably C<sub>2</sub>-C<sub>3</sub> alkylene. When R<sup>4</sup> is a substituted alkyl, hydroxyalkyl, or alkenyl group, and when q is 0, R<sup>5</sup> is preferably a C<sub>2</sub>-C<sub>3</sub> oxyalkylene moiety; when q is 1, R<sup>5</sup> is preferably C<sub>2</sub>-C<sub>3</sub> alkylene.

These ethoxylated cationic polyamines can be derived from polyamino amides such as:



These ethoxylated cationic polyamines can also be derived from polyaminopropyleneoxide derivatives such as:



wherein each c is a number from 2 to about 20.

Carboxylate-containing polyelectrolyte compounds

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An essential component of the invention is one or more carboxylate-containing polyelectrolyte compounds, which have builder or dispersant properties.

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Preferably these compounds are homo- or co-polymeric polycarboxylic compounds and most preferably co-polymeric polycarboxylic compounds in which the acid monomer of said polycarboxylic compound comprises at least two carboxyl groups separated by not more than two carbon atoms. Salts of these polycarboxylic compounds are also considered herein. In a preferred aspect the polycarboxylic compounds of the present invention will comprise at least 12 carboxylate groups.

15

If present in a detergent composition in accord with the present invention the carboxylate-containing polyelectrolyte compound is preferably present at a level of from 0.01% to 40%, more preferably from 0.1% to 10%, most preferably from 0.2% to 6% by weight of the detergent composition

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If present in a detergent component of the present invention the carboxylate-containing polyelectrolyte compound is preferably present at a level of from 0.05% to 30%, more preferably from 0.1% to 15%, more preferably from 0.15% to 7%, most preferably from 0.2% to 2.0% or more preferred to 1.2% by weight of the detergent component.

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Where the component is a spray-dried particle, the carboxylate-containing polyelectrolyte compound is preferably present at a level from 0.2% to 2.0% or more preferred to 1.2% by weight of the spray-dried particle.

30

Such a spray-dried particle or such a component preferably is present in a granular detergent composition at a level of from 5% to 90%, more preferably from 20% to 60%, most preferably from 30% to 50% by weight of the composition.

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The carboxylate-containing polyelectrolyte materials can be prepared by polymerising or copolymerizing suitable unsaturated monomers, preferably in their

acid form. Unsaturated monomeric acids that can be polymerised to form suitable polymeric polycarboxylates are selected from acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in these carboxylate-containing

5 polyelectrolyte compounds herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than 40% by weight. Carboxylate-containing materials can also optionally include further monomeric units such as nonionic spacing units. For example, suitable nonionic spacing units

10 may include vinyl alcohol or vinyl acetate.

Particular preferred carboxylate-containing polyelectrolyte compounds are acrylic/maleic-based co-polymers. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid/ maleic anhydride. The average

15 molecular weight of such copolymers in the acid form preferably can range from 1,000 to 100,000, more preferably from 2,000 to 75,000 or even more preferred to 70,000, but most preferred are the co-polymers with a average molecular weight of from 2,500 to 20,000 or in another preferred embodiment from 60,000 to 75,000 or even 70,000. The ratio of acrylate to maleate segments in such copolymers will

20 generally range from 30:1 to 1:30, more preferably from 10:1 to 1:1, most preferably from 4:1 to 7:3. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915,

25 published December 15, 1982, as well as in EP 193,360, published September 3, 1986.

Other suitable carboxylate-containing polyelectrolyte compounds can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are

30 for example the water-soluble salts of polymerized acrylic acid. The average molecular weight of such homo-polymers in the acid form preferably ranges from 1,800 to 100,000, more preferably from 2,000 to 10,000, most preferably from 3,000 to 5,000. Water-soluble salts of such acrylic acid polymers or can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble

35 polymers of this type are known materials. Use of polyacrylates of this type in

detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Also polyamino-based compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

A further example of carboxylate-containing polyelectrolyte compounds suitable for the purpose of the invention include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Terpolymers containing monomer units selected from maleic acid, acrylic acid and polyaspartic acid, particularly those having an average molecular weight of from 5,000 to 20,000, are also suitable herein.

Further useful carboxylate-containing polyelectrolyte compounds are the polyelectrolyte-containing glycols, particularly those of molecular weight 1,000-10,000, more particularly 2,000 to 8,000 and most preferably about 4,000.

Other preferred carboxylate-containing polyelectrolyte compounds are those which typically have a hydrophilic backbone and at least one hydrophobic side chain.

Preferably this type of carboxylate-containing polyelectrolyte compounds have a molecular weight of between 500 and 100,000, more preferred from 1,000 to 70,000, especially preferred from 1,500 to 10,000, or in another preferred embodiment from 2,800 to 6,000. Carboxylate-containing polyelectrolyte compounds for use herein may for example be prepared by using conventional aqueous polymerisation procedures, suitable methods are for example described in GB 89 24477, GB 89 24478 and GB 89 24479.

Generally the hydrophilic backbone of the polymer is predominantly linear (the main chain of the backbone constitutes at least 50%, preferably more than 75%, most preferred more than 90% by weight of the backbone), suitable monomer constituents of the hydrophilic backbone are for example unsaturated C<sub>1</sub>-C<sub>6</sub> acids, ethers, alcohols, aldehydes, ketones or esters, sugar units, alkoxy units, maleic

anhydride and saturated polyalcohols such as glycerol. Preferably the hydrophobic side groups are composed of alkoxy groups for example butylene oxide and/or propylene oxide and/or alkyl or alkenyl chains having from 5 to 24 carbon atoms. The hydrophobic groups may be connected to the hydrophilic backbone via  
5 relatively hydrophilic bonds for example a poly ethoxy linkage.

Preferred carboxylate-containing polyelectrolyte compounds of this type are the polymers described in WO 91/ 08281.

10 Preferred counterions for the carboxylate-containing polyelectrolyte compounds are for example sodium, magnesium or calcium ions.

#### Spray-dried particle

15 A preferred component according to the invention comprises a spray-dried particle can be used in a detergent composition. The detergent composition may consist essentially of such particles, but preferably the detergent composition comprises the particles and other components, having a different chemical composition.

20 The spray-dried particle of the invention are formed by a process, which includes a spray-drying step. The spray-drying step produces a spray-dried particle, generally having a free-moisture content below 10% by weight, preferably less than 7%, or more preferably less than 6%.

25 As used herein, free-moisture content is determined by placing 2 grams of a sample of base detergent granules in for example a petri dish, placing the sample in a heating chamber up to 160°C for 10 minutes, followed by measurement of the weight loss due to water evaporation.

30 Generally, the particles of the invention are formed in a process whereby a paste or slurry or crutcher mix comprising the cationic compound and the carboxylate-containing polyelectrolytes, is formed into particles and dried in a spray-drying process as known in the art.



The process for manufacturing the spray-dried particles comprises preparing an aqueous solution-dispersion, commonly referred to as a paste or slurry or crutcher mix, comprising the components of the final particle.

- 5 The cationic compound and the carboxylate-containing polyelectrolyte can be mixed together prior to addition to the other ingredients of the crutcher mix, which will be comprised in the spray-dried particle. Alternatively, the cationic compound and the carboxylate-containing polyelectrolyte can be mixed with other organic compounds, which will be comprised in the final spray-dried particle, prior to  
10 addition to the other ingredients of the crutcher mix (which will be comprised in the final spray-dried particle). Alternatively, the cationic compound and the carboxylate-containing polyelectrolyte can be added to the crutcher or crutcher mix at the same time as the other ingredients, which will be comprised in the final spray-dried particle.

15

- To save energy and to increase throughput of the drying equipment the crutcher mix will usually be of as high a solids content as feasible, e.g., 40% to 80%, with the balance, e.g. 10% to 60%, being water. More water may be used but then energy demands are increased, tower throughput are diminished, products resulting  
20 may be tackier and poorer flowing g and often the desired low density base and final detergent composition particles will not be obtained. The crutcher mix preferably has a temperature of from 50°C to 100°C, typically 80°C prior to the drying step.

- 25 The crutcher mix is then sprayed at an elevated pressure (usually from 40 to 100 bar, preferably 70 to 90 bar, typically at about 80 bar) through one or more spray nozzles into a drying tower, through which drying air, passes to dry the resulting droplets of crutcher mix to globular the particles. Instead of spray nozzles, equivalent atomisers of other designs may also be used. The preferred spray tower  
30 design is counter-current, the height of the tower usually being from 5 to 25 meters and the entering hot air, usually the gaseous products of combustion of oil or gas, being at a temperature in the range of from 150° to 400°C and the outlet air usually at a temperature in the range of from 50° to 160°C. Concurrent tower designs may also be employed wherein similar inlet and outlet air temperatures obtain.

35

The nozzle size for producing droplets of crutcher mix will be chosen such particles of the preferred particle size are formed, preferably of from 0.1 mm to 3.0 mm. Preferably, substantially all the particles are within this range when removed from the spray tower, but any off-size particles can be removed by  
5 screening, may be size-reduced to the desired size range or may be recycled in the same or a subsequent crutcher mix.

Preferred additional ingredient of the crutcher mix can be anionic surfactants, cationic softeners or cationic surfactants, nonionic, sulphate and carbonate salts,  
10 and hydrotropes.

Optionally, after drying is complete and the particles in the desired size range are obtained, additional detergent compounds or components can be added to the particles, preferably by melting the compound or component and spraying the  
15 molten compound or component, which may be in concentrated aqueous solution but preferably is free of water, onto the surfaces of the tumbling base particles in an inclined drum, through which the particles progress from an elevation feed end to the discharge end.

20 The particle can be introduced to a detergent composition by any method, known in the art. Preferably, the particles are dry-added to the other detergent ingredients.

#### Additional detergent ingredients

25 The detergent compositions or components in accordance with the invention may also contain additional detergent ingredients. The precise nature of these additional ingredients, and levels of incorporation thereof will depend on the physical form of the component, and the precise nature of the washing operation for which it is to be used.

30

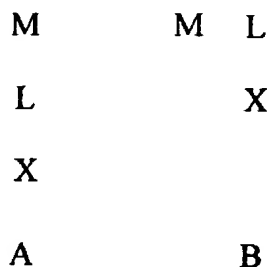
The components or the detergent compositions in accordance with the invention preferably contain one or more additional detergent components selected from surfactants, additional builders, sequestrants, bleach, bleach precursors, bleach catalysts, additional organic polymeric compounds, enzymes, suds suppressors,  
35 additional lime soap dispersants, additional soil suspension and anti-redeposition agents soil releasing agents, perfumes and corrosion inhibitors.

Cationic polymers

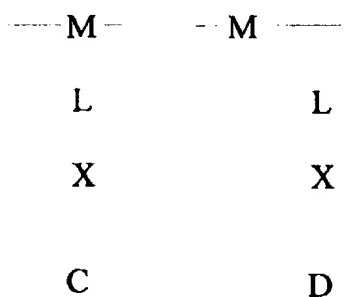
A preferred additional component can be additional polymeric cationic ethoxylated amine compounds with particulate soil/clay-soil removal/ anti-redeposition, selected from the group consisting of water-soluble cationic polymers. These polymers comprise a polymer backbone, at least 2M groups and at least one L-X group, wherein M is a cationic group attached to or integral with the backbone; X is a nonionic group selected from the group consisting of H, C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof; and L is a hydrophilic chain connecting groups M and X or connecting X to the polymer backbone.

As used herein, the term "polymer backbone" refers to the polymeric moiety to which groups M and L-X are attached to or integral with. Included within this term are oligomer backbones (2 to 4 units), and true polymer backbones (5 or more units).

As used herein, the term "attached to " means that the group is pendent from the polymer backbone, examples of which are represented by the following general structures A and B:

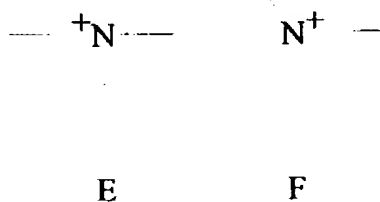


As used herein, the term "integral with" means that the group forms part of the polymer backbone, examples of which are represented by the following general structures C and D:



- Any polymer backbone can be used as long as the cationic polymer formed is water-soluble and has clay soil removal/anti-redeposition properties. Suitable polymer backbones can be derived from the polyurethanes, the polyesters, the polyethers, the polyamides, the polyimides and the like, the polyacrylates, the polyacrylamides, the polyvinylethers, the polyethylenes, the polypropylenes and like polyalkylenes, the polystyrenes and like polyalkarylenes, the polyalkyleneamines, the polyalkyleneimines, the polyvinylamines, the polyalylamines, the polydiallylamines, the polyvinylpyridines, the polyaminotriazoles, polyvinyl alcohol, the aminopolyureylenes, and mixtures thereof.

- M can be any compatible cationic group which comprises an  $N^+$  (quarternary), positively charged center. The quarternary positively charged center can be represented by the following general structures E and F:



- Particularly preferred M groups are those containing a quarternary center represented by general structure E. The cationic group is preferably positioned close to or integral with the polymer backbone.

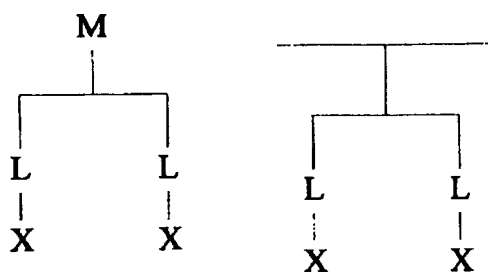
The positive charge of the  $N^+$  centres is offset by the appropriate number of counter anions. Suitable counter anions include  $Cl^-$ ,  $Br^-$ ,  $SO_3^{2-}$ ,  $SO_4^{2-}$ ,  $PO_4^{2-}$ ,  $MeOSO_3^-$  and the like. Particularly preferred counter anions are  $Cl^-$  and  $Br^-$ .

- 5 X can be a nonionic group selected from hydrogen (H),  $C_1$ - $C_4$  alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof. The preferred ester or ether groups are the acetate ester and methyl ether, respectively; The particularly preferred nonionic groups are H and the methyl ether.
- 10 The cationic polymers suitable for use in granular detergent components in accord with the present inventions normally have a ratio of cationic groups M to nonionic groups X of from about 1:1 to about 1:2. However, for example, by appropriate copolymerization of cationic, nonionic (i.e. containing the group L-X), and mixed cationic/nonionic monomers, the ratio of cationic groups M to nonionic groups X
- 15 can be varied. The ratio of groups M to groups X can usually range from about 2:1 to about 1:10. In preferred cationic polymers, the ratio is from about 1:1 to about 1:5. The polymers formed from such copolymerization are typically random, i.e. the cationic, nonionic and mixed cationic/nonionic monomers copolymerize in a non repeating sequence.
- 20 The units which contain groups M and groups L-X can comprise 100% of the cationic polymers of the present invention. However, inclusion of other units (preferably nonionic) in the polymers is also permissible. Examples of other units include acrylamides, vinyl ethers and those containing unquaternized tertiary amine
- 25 groups ( $M^1$ ) containing an N centre. These other units can comprise from 0% to about 90% of the polymer (from about 10% to 100% of the polymer being units containing M and L-X groups, including  $M^1$ -L-X groups). Normally, these other units comprise from 0% to about 50% of the polymer (from about 50% to 100% of the polymer being units containing M and L-X groups).
- 30 The number of groups M and L-X each usually ranges from about 2 to about 200. Typically the number of groups M and L-X are each from about 3 to about 100. Preferably, the number of groups M and L-X are each from about 3 to about 40.
- 35 Other than moieties for connecting groups M and X, or for attachment to the polymer backbone, hydrophilic chain L usually consists entirely of the

polyoxyalkylene moiety  $-(R'O)_m(CH_2CH_2O)_n-$ . The moieties  $-(R'O)_m-$  and  $-(CH_2CH_2O)_n-$  of the polyoxyalkylene moiety can be mixed together, or preferably form blocks of  $-(R'O)_m-$  and  $-(CH_2CH_2O)_n-$  moieties. R' is preferably  $C_3H_6$  (propylene); m is preferably from 0 to about 5, and most preferably 0; i.e. the polyoxyalkylene moiety consists entirely of the moiety  $-(CH_2CH_2O)_n-$ . The moiety  $-(CH_2CH_2O)_n-$  preferably comprises at least about 85% by weight of the polyoxyalkylene moiety, and most preferably 100% by weight (m is 0). For the moiety  $-(CH_2CH_2O)_n-$ , n is usually from about 3 to about 100. Preferably n, is from about 12 to about 42.

10

A plurality (2 or more) of moieties  $-L-X$  can also be hooked together and attached to group M or to the polymer backbone, examples of which are represented by the following general structures G and H:



G

H

15

Structures such as G and H can be formed, for example, by reacting glycidol with group M or with the polymer backbone, and ethoxylating the subsequently formed hydroxy groups.

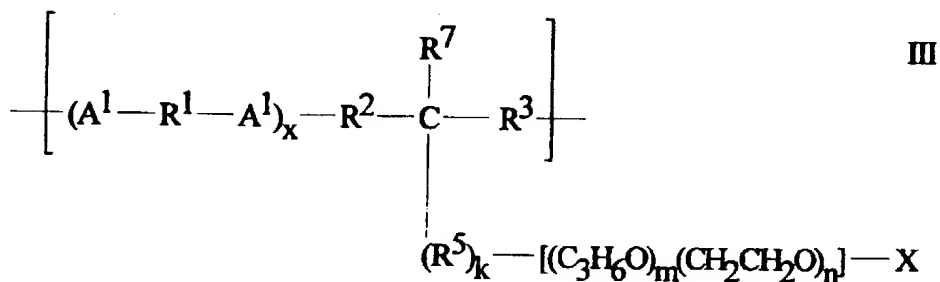
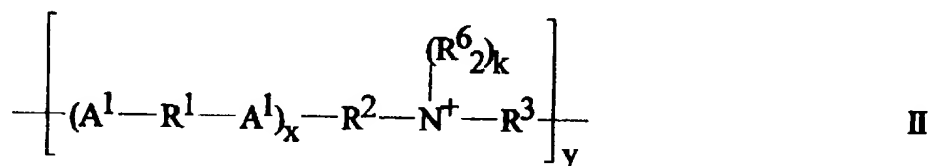
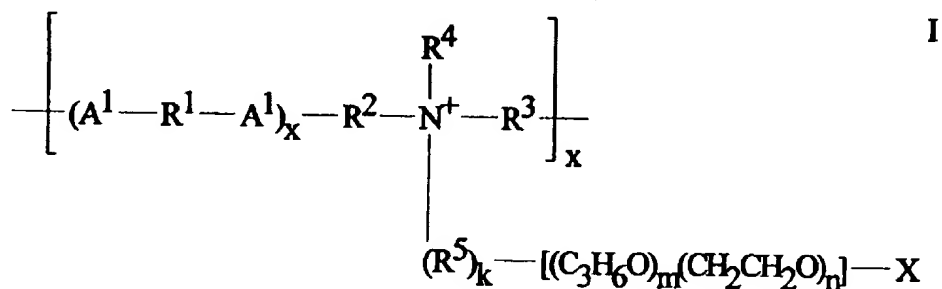
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Representative classes of cationic polymers of the present invention are as follows:

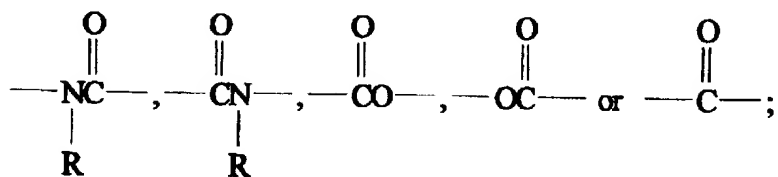
A. Polyurethane, Polyester, Polyether, Polyamide or like Polymers.

25 One class of suitable cationic polymers are derived from polyurethanes, polyesters, polyethers, polyamides and the like. These polymers comprise units selected from those having formulas I, II and III:

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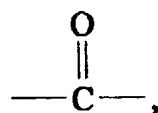


wherein  $A^1$  is



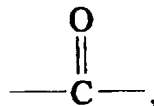
X is 0 or 1; R is H or  $C_1$ - $C_4$  alkyl or hydroxyalkyl;  $R^1$  is  $C_2$ - $C_{12}$  alkylene, hydroxyalkylene, alkenylene, cycloalkylene, arylene or alkarylene, or a  $C_2$ - $C_3$  oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed with  $A^1$ ; when x is 1,  $R^2$  is  $-R^5-$  except when  $A^1$  is

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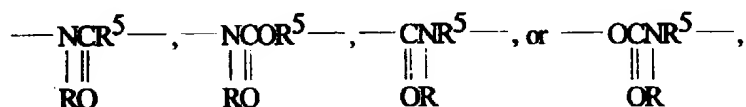
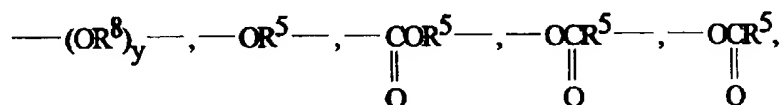
or is  $-(\text{OR}^8)_y-$  or  $-\text{OR}^5-$  provided that no O-O or N-O bonds are formed with  $\text{A}^1$ , and  $\text{R}^3$  is  $-\text{R}^5-$  except when  $\text{A}^1$  is

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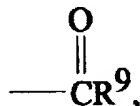
or is  $-(\text{R}^8\text{O})_y-$  or  $-\text{R}^5\text{O}-$  provided that no O-O or O-N bonds are formed with  $\text{A}^1$ ; when  $x$  is 0,  $\text{R}^2$  is

10



and  $\text{R}^3$  is  $-\text{R}^5-$ ;  $\text{R}^4$  is  $\text{C}_1$ - $\text{C}_4$  alkyl or hydroxyalkyl, or the moiety  $-(\text{R}^5)_k-$   $[(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]-\text{X}$ ;  $\text{R}^5$  is  $\text{C}_1$ - $\text{C}_{12}$  alkylene, hydroxyalkylene, alkenylene, arylene, or alkarylene; each  $\text{R}^6$  is  $\text{C}_1$ - $\text{C}_4$  alkyl or hydroxyalkyl, or the moiety  $-(\text{CH}_2)_r\text{A}^2-(\text{CH}_2)_s-$ , wherein  $\text{A}^2$  is  $-\text{O}-$  or  $-\text{CH}_2-$ ;  $\text{R}^7$  is H or  $\text{R}^4$ ;  $\text{R}^8$  is  $\text{C}_2$ - $\text{C}_3$  alkylene or hydroxyalkylene; X is H,

15



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$-\text{R}^9$  or a mixture thereof, wherein  $\text{R}^9$  is  $\text{C}_1$ - $\text{C}_4$  alkyl or hydroxyalkyl; k is 0 or 1; m and n are numbers such that the moiety  $-(\text{CH}_2\text{CH}_2\text{O})_n-$  comprises at least about 85% by weight of the moiety  $[(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]-$ ; m is from 0 to about 5; n is at least about 3; r is 1 or 2, s is 1 or 2, and  $r + s$  is 3 or 4; y is from 2 to

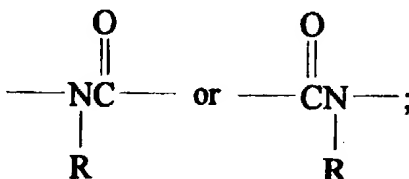
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about 20; the number of u, v and w are such that there are at least 2 N<sup>+</sup> centers and at least 2 X groups.

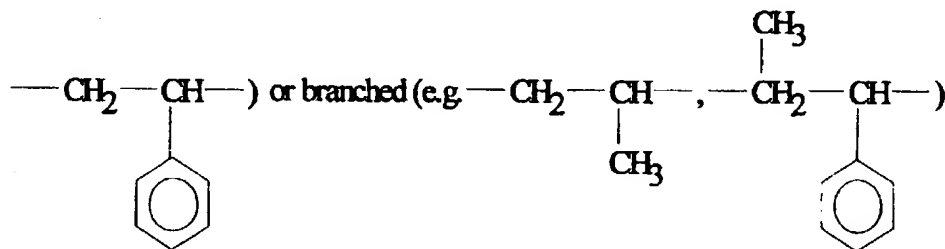
In the above formulas, A<sup>1</sup> is preferably

5



A<sup>2</sup> is preferably -O-; x is preferably 1; and R is preferably H. R<sup>1</sup> can be linear (e.g. -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-,

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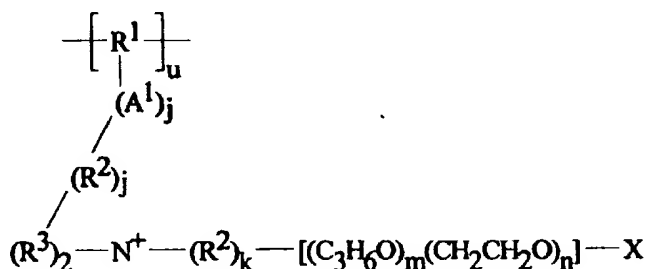
alkylene, hydroxyalkylene, alkenylene, cycloalkylene, alkarylene or oxyalkylene; when R<sup>1</sup> is a C<sub>2</sub>-C<sub>3</sub> oxyalkylene moiety, the number of oxyalkylene units is preferably from about 2 to about 12; R<sup>1</sup> is preferably C<sub>2</sub>-C<sub>6</sub> alkylene or phenylene, and most preferably C<sub>2</sub>-C<sub>6</sub> alkylene (e.g. ethylene, propylene, hexamethylene). R<sup>2</sup> is preferably -OR<sup>5</sup>- or -(OR<sup>8</sup>)<sub>y</sub>-; R<sup>3</sup> is preferably -R<sup>5</sup>O- or -(OR<sup>8</sup>)<sub>y</sub>-; R<sup>4</sup> and R<sup>6</sup> are preferably methyl. Like R<sup>1</sup>, R<sup>5</sup> can be linear or branched, and is preferably C<sub>2</sub>-C<sub>3</sub> alkylene; R<sup>7</sup> is preferably H or C<sub>1</sub>-C<sub>3</sub> alkyl; R<sup>8</sup> is preferably ethylene; R<sup>9</sup> is preferably methyl; X is preferably H or methyl; k is preferably 0; m is preferably 0, r and s are each preferably 2; y is preferably from 2 to about 12.

In the above formulas, n is preferably at least about 6 when the number of N<sup>+</sup> centers and X groups is 2 or 3; n is most preferably at least about 12, with a typical range of about 12 to about 42 for all ranges of u + v + w. For homopolymers (v and w are 0), u is preferably from about 3 to about 20. For random copolymers (u is at least 1 or preferably 0), v and w are each preferably from about 3 to about 40.

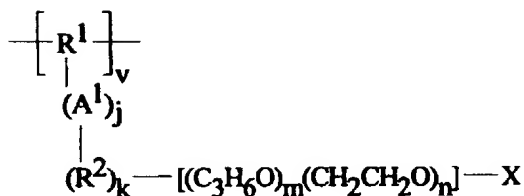
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B. Polyacrylate, Polyacrylamide, Polyvinylether or Like Polymers

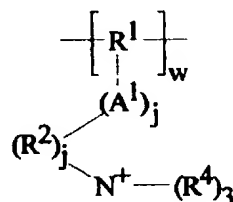
- 5 Another class of suitable cationic polymers are derived from polyacrylates, polyacrylamides, polyvinylethers and the like. These polymers comprise units selected from those having formulas IV, V and VI.



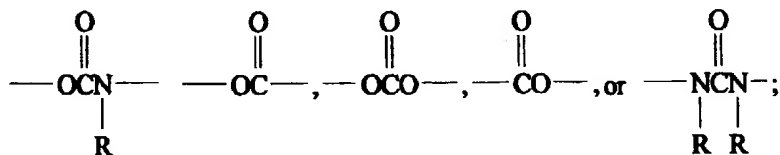
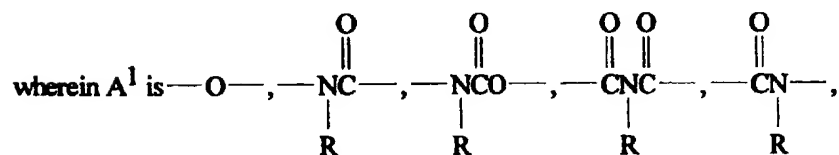
IV



V



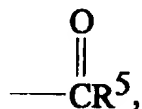
VI



- 10 R is H or  $\text{C}_1$ - $\text{C}_4$  alkyl or hydroxyalkyl;  $\text{R}^1$  is substituted  $\text{C}_2$ - $\text{C}_{12}$  alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or  $\text{C}_2$ - $\text{C}_3$  oxyalkylene; each  $\text{R}^2$  is  $\text{C}_1$ - $\text{C}_{12}$  alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene; each

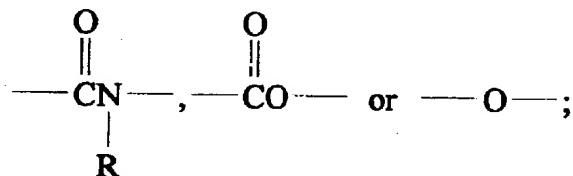
$R^3$  is  $C_1$ - $C_4$  alkyl or hydroxyalkyl, the moiety  $-(R^2)_k-[(C_3H_6O)_m(CH_2CH_2O)_n]-$  X, or together form the moiety  $-(CH_2)_r-A^2-(CH_2)_s-$ , wherein  $A^2$  is  $-O-$  or  $-CH_2-$ ; each  $R^4$  is  $C_1$ - $C_4$  alkyl or hydroxyalkyl, or two  $R^4$  together form the moiety  $-(CH_2)_r-A^2-(CH_2)_s-$ ; X is H,

5



$-R^5$  or mixture thereof, wherein  $R^5$  is  $C_1$ - $C_4$  alkyl or hydroxalkyl; j is 1 or 0; k is 1 or 0; m and n are numbers such that the moiety  $-(CH_2CH_2O)_n-$  comprises at least about 85% by weight of the moiety  $-(C_3H_6O)_m(CH_2CH_2O)_n-$ ; m is from 0 to about 5; n is at least about 3; r is 1 or 2, s is 1 or 2 and  $r + s$  is 3 or 4; the number of u, v and w are such that there are at least  $2N +$  centres and at least 2 X groups.

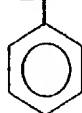
15 In the above formulas,  $A^1$  is preferably



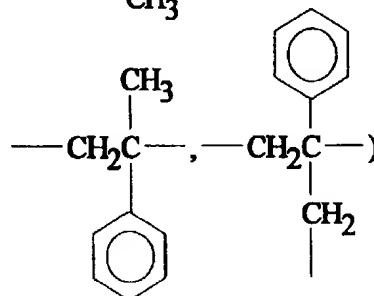
$A^2$  is preferably  $-O-$ ; R is preferably H.  $R^1$  can be linear

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(e.g.  $\text{—CH}_2\text{—CH—CH}_2\text{—}$ ,  $\text{—CH}_2\text{CH—}$ ) or

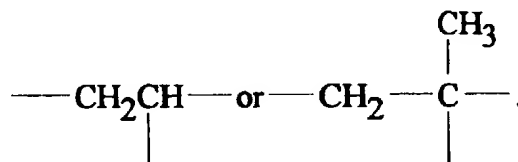


branched (e.g.  $\text{—CH}_2\text{—C—}$ ,  $\text{—CH}_2\text{CH—}$ ,  
 $\text{CH}_3$   
 $\text{CH}_3$



substituted alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene;  $R^1$  is preferably substituted  $C_2\text{—}C_6$  alkylene or substituted  $C_2\text{—}C_3$  oxyalkylene, and most preferably

5



Each  $R^2$  is preferably  $C_2\text{—}C_3$  alkylene, each  $R^3$  and  $R^4$  are preferably methyl;  $R^5$  is preferably methyl; X is preferably H or methyl; j is preferably 1; k is preferably 0; m is preferably 0; r and s are each preferably 2.

10

In the above formulas, n, u, v and w can be varied according to the n, u, v and w for the polyurethane and like polymers.

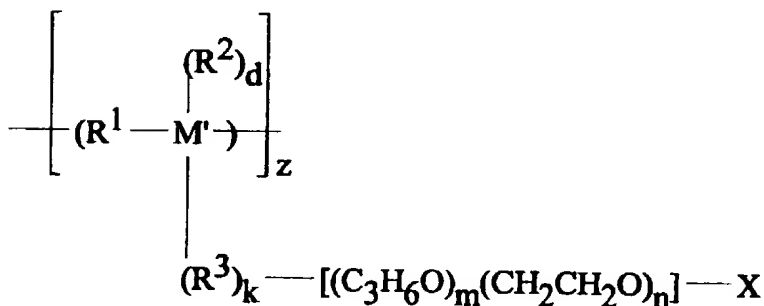
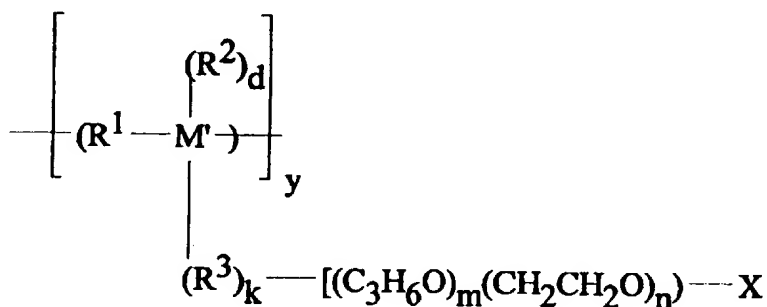
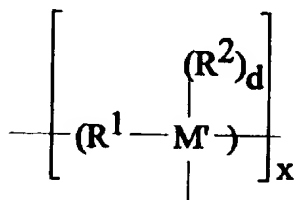
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C. Polyalkyleneamine, Polyalkyleneimine or like polymers.

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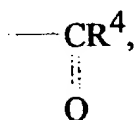
Another class of suitable cationic polymers are derived from polyalkyleneamines, polyalkyleneimines and the like. These polymers comprise units selected from those having formulas VII and VIII and IX.

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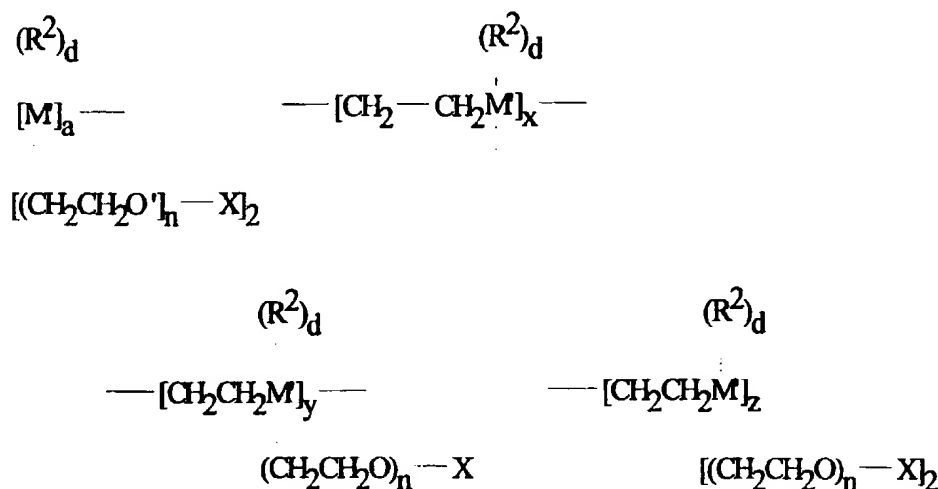


- wherein  $R^1$  is  $C_2$ - $C_{12}$  alkylene, hydroxyalkylene, alkenylene, cycloalkylene, arylene or alkarylene, or a  $C_2$ - $C_3$  oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each  $R^2$  is  $C_1$ - $C_4$  alkyl or hydroxyalkyl, or the moiety  $-(R^3)_k - [(C_3H_6O)_m(CH_2CH_2O)_n] - X$ ;  $R^3$  is  $C_1$ - $C_{12}$  alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene;  $M'$  is an N+ or N centre; X is H,

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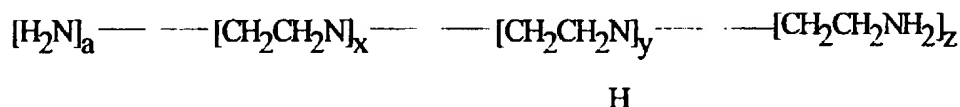


- 5  $\text{---R}^4$  or mixture thereof, wherein  $\text{R}^4$  is  $\text{C}_1\text{--C}_4$  alkyl or hydroxyalkyl; d is 1 when  $\text{M}'$  is  $\text{N}^+$  and is 0 when  $\text{M}'$  is  $\text{N}$ ; e is 2 when  $\text{M}'$  is  $\text{N}^+$  and is 1 when  $\text{M}'$  is  $\text{N}$ ; k is 1 or 0; m and n are numbers such that the moiety  $\text{---}(\text{CH}_2\text{CH}_2\text{O})_n\text{---}$  comprises at least about 85% by weight of the moiety  $\text{---}[(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]\text{---}$ ; m is from 0 to about 5; n is at least about 3; the number of x, y and z are such that there are at least  $2\text{M}'$  groups, at least  $2\text{N}^+$  centres and at least 2 X groups.
- 10 In the above formulas,  $\text{R}^1$  can be varied like  $\text{R}^1$  of the polyurethane and like polymers; each  $\text{R}^2$  is preferably methyl or the moiety  $\text{---}(\text{R}^3)_k\text{---}$   $[(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]\text{---X}$ ;  $\text{R}^3$  is preferably  $\text{C}_2\text{--C}_3$  alkylene;  $\text{R}^4$  is preferably methyl; X is preferably H; k is preferably 0; m is preferably 0.
- 15 In the above formulas, n is preferably at least about 6 when the number of  $\text{M}'$  and X groups is 2 or 3; n is most preferably at least about 12, with a typical range of from about 12 to about 42 for all ranges of  $x + y + z$ . Typically,  $x + y + z$  is from 2 to about 40 and preferably from 2 to about 20. For short chain length polymers,  $x + y + z$  can range from 2 to 9 with from 2 to 9  $\text{N}^+$  centres and from
- 20 2 to 11 X groups. For long chain length polymers,  $x + y + z$  is at least 10, with a preferred range of from 10 to about 42. For the short and long chain length polymers, the  $\text{M}'$  groups are typically a mixture of from about 50 to 100%  $\text{N}^+$  centres and from 0 to about 50% N centres.
- 25 Preferred cationic polymers within this class are derived from the  $\text{C}_2\text{--C}_3$  polyalkyleneamines ( $x + y + z$  is from 2 to 9) and polyalkyleneimines ( $x + y + z$  is at least 10, preferably from 10 to about 42). Particularly preferred cationic polyalkyleneamines and polyalkyleneimines are the cationic polyethyleneamines (PEA's) and polyethyleneimines (PEI's). These preferred cationic polymers
- 30 comprise units having the general formula:



wherein  $R^2$  (preferably methyl),  $M'$ ,  $X$ ,  $d$ ,  $x$ ,  $y$ ,  $z$  and  $n$  are defined as before;  $a$  is 1 or 0.

- 5 Prior to ethoxylation, the PEAs used in preparing cationic polymers of the present invention have the following general formula:



- wherein  $x + y + z$  is from 2 to 9, and  $a$  is 0 or 1 (molecular weight of from about 100 to about 400). Each hydrogen atom attached to each nitrogen atom represents an active site for subsequent ethoxylation. For preferred PEAs,  $x + y + z$  is from about 3 to about 7 (molecular weight is from about 140 to about 310). These PEA's can be obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are
- 15 triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms
- 20 appear. See US Pat. No. 2,792,372 to Dickson, issues May 14, 1957, which describes the preparation of PEAs.

The minimum degree of ethoxylation required for preferred clay soil removal/anti-redeposition performance can vary depending upon the number of units in the

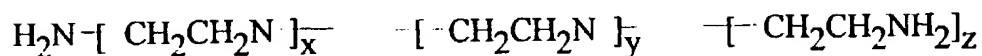
PEA. Where  $y + z$  is 2 or 3,  $n$  is preferably at least about 6. Where  $y + z$  is from 4 to 9, suitable benefits are achieved when  $n$  is at least about 3. For preferred cationic PEAs,  $n$  is at least about 12, with a typical range of about 12 to about 42.

5

The PEIs used in preparing the polymers of the present invention have a molecular weight of at least about 440 prior to ethoxylation, which represents at least about 10 units. Preferred PEIs used in preparing these polymers have a molecular weight of from about 600 to about 1800. The polymer backbone of these PEIs can be represented by the general formula:

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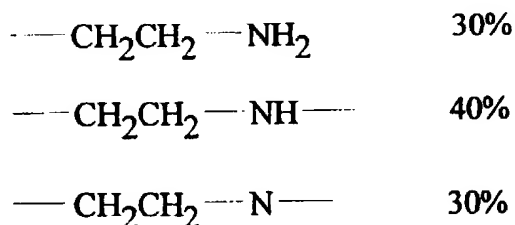
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wherein the sum of  $x$ ,  $y$ , and  $z$  represents a number of sufficient magnitude to yield a polymer having the molecular weights previously specified. Although linear polymer backbones are possible, branch chains can also occur. The relative proportions of primary, secondary and tertiary amine groups present in the polymer can vary, depending on the manner of preparation. The distribution of amine groups is typically as follows:

20



25

Each hydrogen atom attached to each nitrogen atom of the PEI represents an active site for subsequent ethoxylation. These PEIs can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing PEIs are disclosed in US Pat. No. 2,182,306 to Ulrich et al., issued Dec. 5, 1939; US Pat No. 3,033,746 to Mayle et al.,



issued May 8, 1962; US Pat. No. 2,208,095 to Esselmann et al., issued July 16, 1940; US Pat. No. 2,806,839 to Crowther, issued Sept. 17, 1957; and US Pat. No. 2,533,696 to Wilson, issued May 21, 1951 (all herein incorporated by reference).

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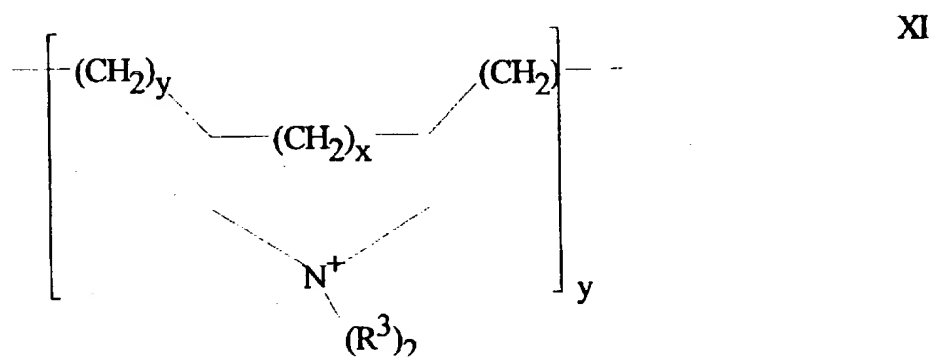
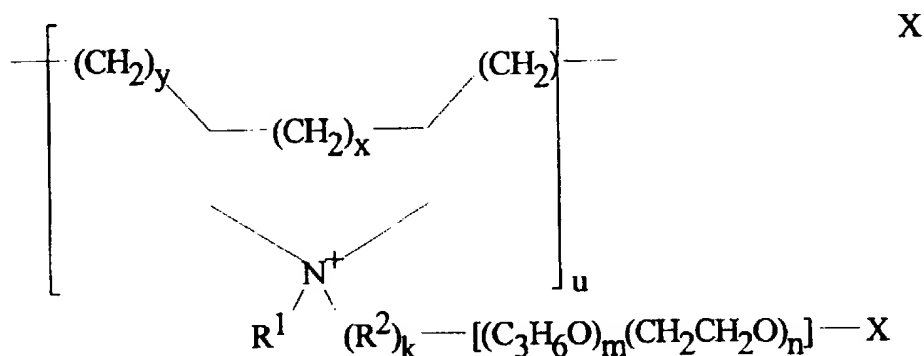
As defined in the preceding formulas,  $n$  is at least about 3 for the cationic PEIs. However, it should be noted that the minimum degree of ethoxylation required for suitable clay soil removal/anti-redeposition performance can increase as the molecular weight of the PEI increases, especially much beyond about 1800. Also, the degree of ethoxylation for preferred polymers increases as the molecular weight of the PEI increases. For PEIs having a molecular weight of at least about 600,  $n$  is preferably at least about 12, with a typical range of from about 12 to about 42. For PEIs having a molecular weight of at least 1800,  $n$  is preferably at least about 24, with a typical range of from about 24 to about 42.

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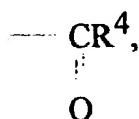
#### D. Diallylamine Polymers

Another class of suitable cationic polymers are those derived from the diallylamines. These polymers comprise units selected from those having formulas X and XI:

20



wherein  $\text{R}^1$  is  $\text{C}_1$ - $\text{C}_4$  alkyl or hydroxyalkyl, or the moiety  $-(\text{R}^2)_k-$   
 $[(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]-\text{X}$ ;  $\text{R}^2$  is  $\text{C}_1$ - $\text{C}_{12}$  alkylene, hydroxyalkylene, alkylene,  
 5 arylenes or alkarylenes; each  $\text{R}^3$  is  $\text{C}_1$ - $\text{C}_4$  alkyl or hydroxyalkyl, or together form  
 the moiety  $-(\text{CH}_2)_r\text{A}-(\text{CH}_2)_s-$ , wherein A is  $-\text{O}-$  or  $-\text{CH}_2-$ ; X is H,



10  $-\text{R}^4$  or mixture thereof, wherein  $\text{R}^4$  is  $\text{C}_1$ - $\text{C}_4$  alkyl or hydroxyalkyl; k is 1 or 0;  
 m and n are numbers such that the moiety  $-(\text{CH}_2\text{CH}_2\text{O})_n-$  comprises at least about  
 85% by weight of the moiety  $-(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n-$ ; m is from 0 to about 5;  
 n is at least about 3; r is 1 or 2, s is 1 or 2, and  $r + s$  is 3 or 4; x is 1 or 0; y is  
 1 when x is 0 and 0 when x is 1; the number of u and v are such that there are at  
 15 least  $2N +$  centres and at least 2 X groups.

In the above formulas, A is preferably -O-;  $R^1$  is preferably methyl; each  $R^2$  is preferably  $C_2-C_3$  alkylene; each  $R^3$  is preferably methyl;  $R^4$  is preferably methyl; X is preferably H; k is preferably 0; m is preferably 0; r and s are each preferably 2.

5

In the above formulas, n is preferably at least about 6 when the number of N+ centres and X groups are each 2 or 3, n is preferably at least 12, with a typical range of from about 12 to about 42 for all range of u + v. Typically, v is 0, and u is from 2 to about 40, and preferably from 2 to about 20.

10

#### Additional surfactant

The detergent compositions or components preferably contain an additional surfactant selected from anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

15

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

20

Where present, ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

25

#### Anionic surfactant

The detergent compositions or components preferably comprise an additional anionic surfactant. Essentially any anionic surfactants useful for deterative purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

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35

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C<sub>6</sub>-C<sub>14</sub> diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

#### Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C<sub>5</sub>-C<sub>17</sub> acyl-N-(C<sub>1</sub>-C<sub>4</sub> alkyl) and -N-(C<sub>1</sub>-C<sub>2</sub> hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C<sub>10</sub>-C<sub>18</sub> alkyl sulfates, more preferably the C<sub>11</sub>-C<sub>15</sub> branched chain alkyl sulfates and the C<sub>12</sub>-C<sub>14</sub> linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C<sub>10</sub>-C<sub>18</sub> alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C<sub>11</sub>-C<sub>18</sub>, most preferably C<sub>11</sub>-C<sub>15</sub> alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

#### Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C<sub>5</sub>-C<sub>20</sub> linear alkylbenzene sulfonates, alkyl ester sulfonates, C<sub>6</sub>-C<sub>22</sub> primary or secondary alkane sulfonates, C<sub>6</sub>-C<sub>24</sub> olefin sulfonates, sulfonated polycarboxylic

acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

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Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

- 10 Suitable alkyl ethoxy carboxylates include those with the formula  $RO(CH_2CH_2O)_xCH_2COO^-M^+$  wherein R is a  $C_6$  to  $C_{18}$  alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula  $RO-(CHR_1-CHR_2-$   
15  $O)-R_3$  wherein R is a  $C_6$  to  $C_{18}$  alkyl group, x is from 1 to 25,  $R_1$  and  $R_2$  are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and  $R_3$  is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

20

- Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

25

Alkali metal sarcosinate surfactant

- 30 Other suitable anionic surfactants are the alkali metal sarcosinates of formula  $R-CON(R^1)CH_2COOM$ , wherein R is a  $C_5$ - $C_{17}$  linear or branched alkyl or alkenyl group,  $R^1$  is a  $C_1$ - $C_4$  alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

35

Alkoxyated nonionic surfactant

Essentially any alkoxyated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

- 5 Preferred alkoxyated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

10

Nonionic alkoxyated alcohol surfactant

- 15 The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

20

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula  $R^2CONR^1Z$  wherein :  $R^1$  is H,  $C_1$ - $C_4$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable  $C_1$ - $C_4$  alkyl, more preferably  $C_1$  or  $C_2$  alkyl, most preferably  $C_1$  alkyl (i.e., methyl); and  $R^2$  is a  $C_5$ - $C_{31}$  hydrocarbyl, preferably straight-chain  $C_5$ - $C_{19}$  alkyl or alkenyl, more preferably straight-chain  $C_9$ - $C_{17}$  alkyl or alkenyl, most preferably straight-chain  $C_{11}$ - $C_{17}$  alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

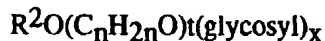
15 Nonionic fatty acid amide surfactant

Suitable fatty acid amide surfactants include those having the formula:  $R^6CON(R^7)_2$  wherein  $R^6$  is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each  $R^7$  is selected from the group consisting of hydrogen,  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl, and  $-(C_2H_4O)_xH$ , where x is in the range of from 1 to 3.

Nonionic alkylpolysaccharide surfactant

25 Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

30 Preferred alkylpolyglycosides have the formula



wherein  $R^2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups

contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

#### Amphoteric surfactant

5

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

10 Suitable amine oxides include those compounds having the formula  $R^3(OR^4)_xN^0(R^5)_2$  wherein  $R^3$  is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each  $R^5$  is an alkyl or hydroxyalkyl group containing from 1 to 3, or a  
15 polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C<sub>10</sub>-C<sub>18</sub> alkyl dimethylamine oxide, and C<sub>10</sub>-18 acylamido alkyl dimethylamine oxide.

20 A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

#### Zwitterionic surfactant

25 Zwitterionic surfactants can also be incorporated into the detergent compositions or components. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

30

Suitable betaines are those compounds having the formula  $R(R')_2N^+R^2COO^-$  wherein R is a C<sub>6</sub>-C<sub>18</sub> hydrocarbyl group, each  $R^1$  is typically C<sub>1</sub>-C<sub>3</sub> alkyl, and  $R^2$  is a C<sub>1</sub>-C<sub>5</sub> hydrocarbyl group. Preferred betaines are C<sub>12</sub>-18 dimethyl-ammonio hexanoate and the C<sub>10</sub>-18 acylamidopropane (or ethane) dimethyl (or  
35 diethyl) betaines. Complex betaine surfactants are also suitable for use herein.



Cationic surfactants

Preferably, if a cationic surfactant is present, the cationic surfactant is selected from the group consisting of cationic mono-alkoxylated amine surfactants, cationic  
 5 bis-alkoxylated amine surfactants and mixtures thereof.

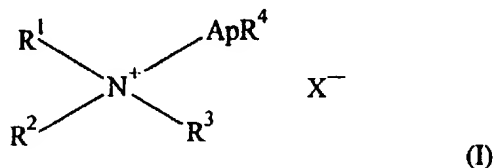
The cationic surfactant is preferably present at a level of from 0.1% to 20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3% by weight of the detergent composition.

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Cationic mono-alkoxylated amine surfactants

The cationic surfactant can be a cationic mono-alkoxylated amine surfactant, which has the general formula I:

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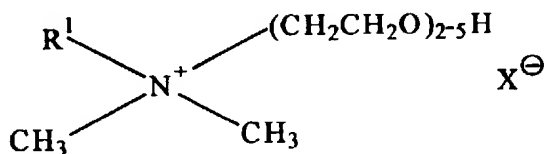


wherein  $R^1$  is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about  
 20 6 to about 14 carbon atoms;  $R^2$  and  $R^3$  are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl, most preferably both  $R^2$  and  $R^3$  are methyl groups;  $R^4$  is selected from hydrogen (preferred), methyl and ethyl;  $X^-$  is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is a alkoxy  
 25 group, especially a ethoxy, propoxy or butoxy group; and p is from 0 to about 30, preferably 2 to about 15, most preferably 2 to about 8, with the proviso that if A is ethoxy and  $R^4$  is hydrogen and p is 1,  $R^1$  is not a  $C_{12}$ - $C_{14}$  alkyl group.

Preferably the  $ApR^4$  group in formula I has  $p=1$  and is a hydroxyalkyl group,  
 30 having no greater than 6 carbon atoms whereby the —OH group is separated from the quaternary ammonium nitrogen atom by no more than 3 carbon atoms. Particularly preferred  $ApR^4$  groups are — $CH_2CH_2OH$ , — $CH_2CH_2CH_2OH$ , — $CH_2CH(CH_3)OH$  and — $CH(CH_3)CH_2OH$ , with — $CH_2CH_2OH$  being

particularly preferred. Preferred  $R^1$  groups have no greater than 10 carbon atoms, or even no greater than 8 or 9 carbon atoms. Preferred  $R^1$  groups are linear alkyl groups. Linear  $R^1$  groups having from 8 to 11 carbon atoms, or from 8 to 10 carbon atoms are preferred. Such a cationic surfactant which is highly preferred  
 5 has a formula wherein  $R^1$  is a C<sub>8</sub>-C<sub>10</sub> alkyl group, p is 1, A is ethoxy and  $R_2$  and  $R_3$  are methyl groups.

Another highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula

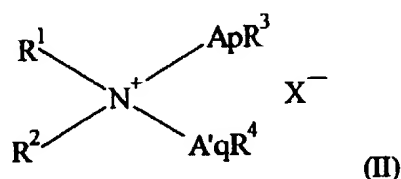


10 wherein  $R^1$  is C<sub>10</sub>-C<sub>18</sub> hydrocarbyl and mixtures thereof, especially C<sub>10</sub>-C<sub>14</sub> alkyl, preferably C<sub>10</sub> and C<sub>12</sub> alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

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#### Cationic bis-alkoxylated amine surfactant

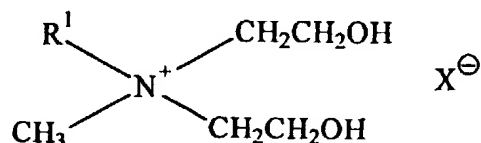
20 The cationic surfactant can also be a cationic bis-alkoxylated amine surfactant, which has the general formula II:



wherein  $R^1$  is an alkyl or alkenyl moiety containing from about 8 to about 18  
 25 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms;  $R^2$  is an alkyl group containing from one to three carbon atoms, preferably methyl;  $R^3$  and  $R^4$  can vary independently and are selected from hydrogen (preferred), methyl and ethyl,  $X^-$  is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide  
 30 electrical neutrality. A and A' can vary independently and are each selected from

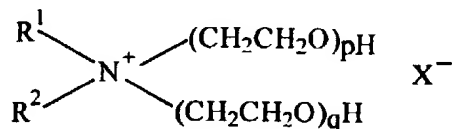
C<sub>1</sub>-C<sub>4</sub> alkoxy, especially ethoxy, (i.e., -CH<sub>2</sub>CH<sub>2</sub>O-), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

- 5 Highly preferred cationic bis-alkoxylated amine surfactants for use herein are of the formula



- wherein R<sup>1</sup> is C<sub>10</sub>-C<sub>18</sub> hydrocarbyl and mixtures thereof, preferably C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub> alkyl and mixtures thereof. X is any convenient anion to provide charge  
 10 balance, preferably chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in a preferred compound R<sup>1</sup> is derived from (coconut) C<sub>12</sub>-C<sub>14</sub> alkyl fraction fatty acids, R<sup>2</sup> is methyl and ApR<sup>3</sup> and A'qR<sup>4</sup> are each monoethoxy.

- 15 Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:



- wherein R<sup>1</sup> is C<sub>10</sub>-C<sub>18</sub> hydrocarbyl, preferably C<sub>10</sub>-C<sub>14</sub> alkyl, independently p is 1 to about 3 and q is 1 to about 3, R<sup>2</sup> is C<sub>1</sub>-C<sub>3</sub> alkyl, preferably methyl, and X is  
 20 an anion, especially chloride or bromide.

- Other compounds of the foregoing type include those wherein the ethoxy (CH<sub>2</sub>CH<sub>2</sub>O) units (EO) are replaced by butoxy (Bu) isopropoxy [CH(CH<sub>3</sub>)CH<sub>2</sub>O] and [CH<sub>2</sub>CH(CH<sub>3</sub>)O] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO  
 25 and/or Pr and/or i-Pr units.

Water-soluble builder compound

The detergent components or compositions can contain additional water-soluble builder compounds.

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Suitable water-soluble builder compounds include carboxylate materials, borates, phosphates, and mixtures of any of the foregoing.

10

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

15

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

20

The carboxylate builder suitable for use in the detergent composition or components thereof can be monomeric or oligomeric (containing up to four carboxylate groups) in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

25

Suitable, additional carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Carboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Carboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

35

Carboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Carboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent  
5 Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred additional carboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

- 10 The parent acids of the monomeric or dimeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Partially soluble or insoluble builder compound

15

The detergent component or compositions may contain a partially soluble or insoluble builder compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

20

Examples of largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula  $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$  wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5  
25 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

- 30 The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula

35  $\text{Na}_{12} [\text{AlO}_2]_{12} (\text{SiO}_2)_{12} \cdot x\text{H}_2\text{O}$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$ .

Another preferred aluminosilicate zeolite is zeolite MAP builder.

- 5 The zeolite MAP can be present at a level of from 1% to 80%, more preferably from 15% to 40% by weight of the compositions.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to  
10 aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

15

In a preferred aspect the zeolite MAP detergent builder has a particle size, expressed as a  $d_{50}$  value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres.

- 20 The  $d_{50}$  value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer. Other methods of establishing  $d_{50}$  values are disclosed in EP 384070A.

25

#### Heavy metal ion sequestrant

- The detergent components or compositions preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is  
30 meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

- 5     Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

- 10     Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

- Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid,  
15     ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

- 20     Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-  
25     hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The  $\beta$ -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

- 30     EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG) and  
35     2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

### Organic peroxyacid bleaching system

A preferred feature of detergent compositions or components is an organic peroxyacid bleaching system. In one preferred execution the bleaching system  
5 contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into  
10 the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

### Inorganic perhydrate bleaches

15 Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

20 Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts  
25 however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

30 Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula  $\text{NaBO}_2\text{H}_2\text{O}_2$  or the tetrahydrate  $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ .

35 Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a

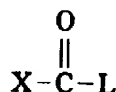


formula corresponding to  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ , and is available commercially as a crystalline solid.

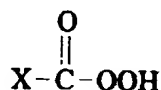
Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions or components thereof.

#### Peroxyacid bleach precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the detergent compositions.

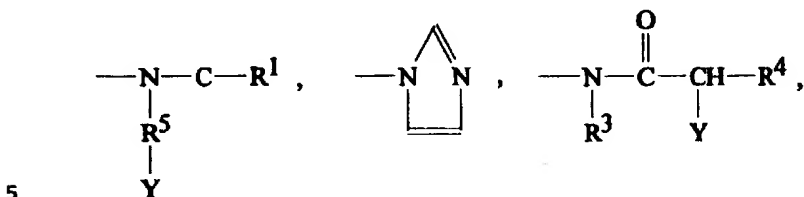
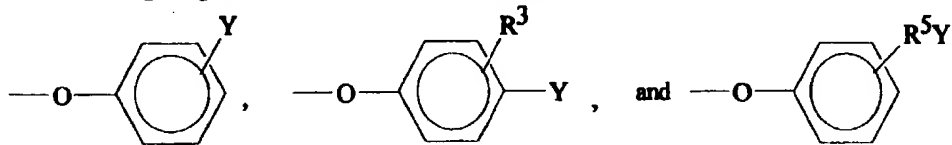
Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

#### Leaving groups

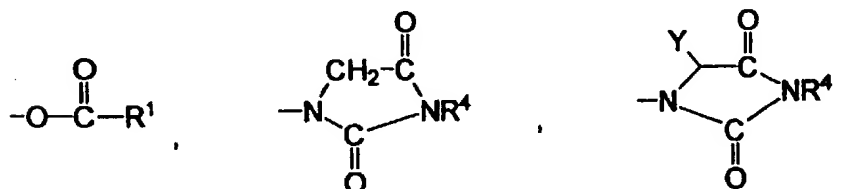
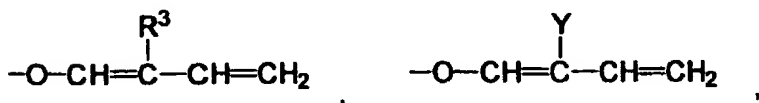
The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash

cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:



5



10

and mixtures thereof, wherein  $R^1$  is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms,  $R^3$  is an alkyl chain containing from 1 to 8 carbon atoms,  $R^4$  is H or  $R^3$ ,  $R^5$  is an alkenyl chain containing from 1 to 8 carbon atoms and Y is H or a solubilizing group. Any of  $R^1$ ,  $R^3$  and  $R^4$  may be substituted by

essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups

15

The preferred solubilizing groups are  $\text{---SO}_3^-\text{M}^+$ ,  $\text{---CO}_2^-\text{M}^+$ ,  $\text{---SO}_4^-\text{M}^+$ ,  $\text{---N}^+(\text{R}^3)_4\text{X}^-$  and  $\text{O---N}(\text{R}^3)_3$  and most preferably  $\text{---SO}_3^-\text{M}^+$  and  $\text{---CO}_2^-\text{M}^+$

wherein  $R^3$  is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

#### Alkyl percarboxylic acid bleach precursors

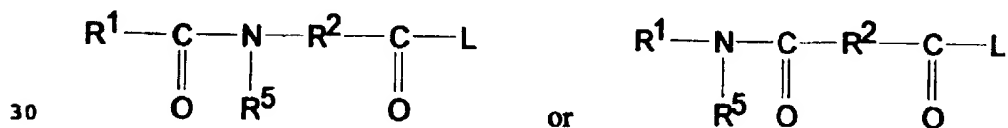
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N<sup>1</sup>N<sup>1</sup> tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-trimethyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

#### Amide substituted alkyl peroxyacid precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein  $R^1$  is an alkyl group with from 1 to 14 carbon atoms,  $R^2$  is an alkylene group containing from 1 to 14 carbon atoms, and  $R^5$  is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide

substituted bleach activator compounds of this type are described in EP-A-0170386.

#### Perbenzoic acid precursor

5 Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the  
10 imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

#### Cationic peroxyacid precursors

15 Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

20 Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors  
25 are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as  
30 described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter

Cationic peroxyacid precursors are described in U.S. Patents 4,904,406;  
35 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

5

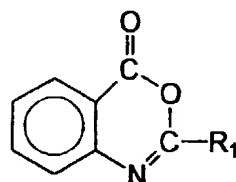
Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

10

#### Benzoxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

15



20

wherein  $R_1$  is H, alkyl, alkaryl, aryl, or arylalkyl.

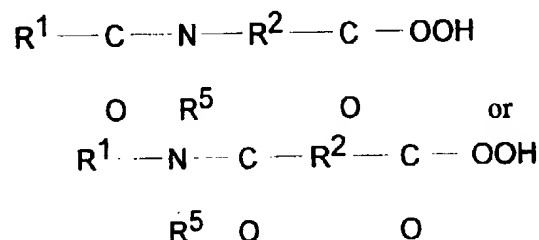
#### Preformed organic peroxyacid

25

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

30

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



5 wherein R<sup>1</sup> is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R<sup>2</sup> is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R<sup>5</sup> is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

10 Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable  
15 herein.

### Enzyme

20 Another preferred ingredient useful in the detergent compositions or components is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available cellulases, endolases, cutinases, lipases, amylases, neutral and alkaline proteases, esterases, pectinases, lactases and peroxidases conventionally incorporated into  
25 detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo  
30 Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the

invention at a level of from 0.0001 % to 4 % active enzyme by weight of the composition.

Preferred amylases include, for example,  $\alpha$ -amylases obtained from a special strain  
5 of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred  
commercially available amylases include for example, those sold under the  
tradename Rapidase by Gist-Brocades, and those sold under the tradename  
Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be  
incorporated into the composition in accordance with the invention at a level of  
10 from 0.0001 % to 2 % active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from  
0.0001 % to 2 % by weight, preferably 0.001 % to 1 % by weight, most preferably  
from 0.001 % to 0.5 % by weight of the compositions.

15

The lipase may be fungal or bacterial in origin being obtained, for example, from a  
lipase producing strain of *Humicola* sp., *Thermomyces* sp. or *Pseudomonas* sp.  
including *Pseudomonas pseudoalcaligenes* or *Pseudomas fluorescens*. Lipase from  
chemically or genetically modified mutants of these strains are also useful herein.

20

A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is  
described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from *Humicola*  
*lanuginosa* and expressing the gene in *Aspergillus oryza*, as host, as described in  
25 European Patent Application, EP-A-0258 068, which is commercially available  
from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase.  
This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued  
March 7, 1989.

30

#### Suds suppressing system

The detergent components or compositions when formulated for use in machine  
washing compositions, preferably comprise a suds suppressing system present at a  
level of from 0.01 % to 15 %, preferably from 0.05 % to 10 %, most preferably  
35 from 0.1 % to 5 % by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

- 5 By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

10 Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred  
15 silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued  
20 September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

25 Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C<sub>18</sub>-C<sub>40</sub> ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine chlortriazines formed as  
30 products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

35 A preferred suds suppressing system comprises



(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C<sub>16</sub>-C<sub>18</sub> ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

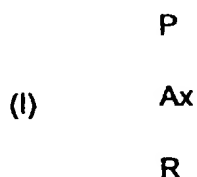
Polymeric dye transfer inhibiting agents

The detergent components or compositions may also comprise from 0.01% to 10%, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

- 5 The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these polymers can be cross-linked polymers..

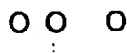
10 a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



15

wherein P is a polymerisable unit, and

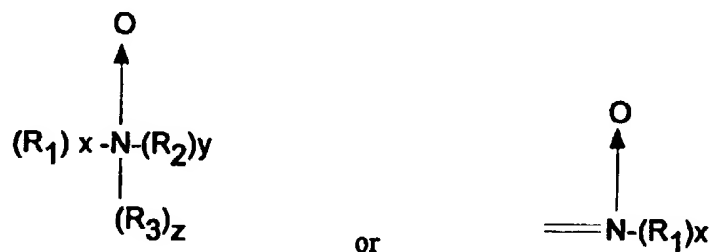


A is NC, CO, C, -O-, -S-, -N-; x is 0 or 1;

20

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

- 25 The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

- Suitable herein are copolymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred
- 5 copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The detergent components or compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinylloxazolidone

The detergent components or compositions herein may also utilize polyvinylloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinylloxazolidones have an average molecular weight of from 2,500 to 400,000.

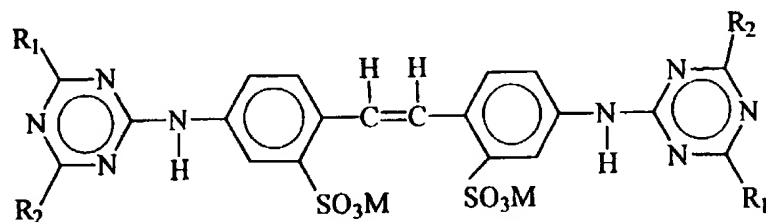
e) Polyvinylimidazole

The detergent components or compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical brightener

The detergent components or compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein  $R_1$  is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl;  $R_2$  is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula,  $R_1$  is anilino,  $R_2$  is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula,  $R_1$  is anilino,  $R_2$  is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula,  $R_1$  is anilino,  $R_2$  is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

#### Polymeric Soil Release Agent

30

Known polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present detergent components or compositions. If utilized, SRA's

will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

10

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-

5 sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

10 SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C<sub>1</sub>-C<sub>4</sub> alkyl celluloses and C<sub>4</sub> hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) 15 per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

20

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal 25 hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. 30 See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.;

Other optional ingredients



Other optional ingredients suitable for inclusion in the components or compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

### Near neutral wash pH detergent formulation

While the detergent components and particularly the detergent compositions comprising the components are operative within a wide range of wash pHs (e.g. from about 5 to about 12), they are particularly suitable when formulated to provide a near neutral wash pH, i.e. an initial pH of from about 7.0 to about 10.5 at a concentration of from about 0.1 to about 2% by weight in water at 20°C. Near neutral wash pH formulations are better for enzyme stability and for preventing stains from setting. In such formulations, the wash pH is preferably from about 7.0 to about 10.5, more preferably from about 8.0 to about 10.5, most preferably from 8.0 to 9.0.

Preferred near neutral wash pH detergent formulations are disclosed to European Patent Application 83.200688.6, filed May 16, 1983, J.H.M. Wertz and P.C.E. Goffinet.

Highly preferred components or compositions of this type also preferably contain from about 2 to about 10% by weight of citric acid and minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, such as salts of toluene sulphonate, xylene sulphonate or cumene sulphonate, enzyme stabilizing agents, suds regulants, opacifiers, anti-oxidants, bactericides, dyes, perfumes and brighteners, such as those described in US Patent 4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference).

### Form of the component and the compositions

The detergent component of the invention can be made via a variety of methods, including agglomeration or extrusion of a mixture of the various compounds comprised, or to be comprised in the detergent component, but preferably via spray-drying of a mixture or slurry comprising the water-soluble cationics and the carboxylate-containing polyelectrolyte compounds. This can be done via any method of spray-drying, known in the art. Thus, the detergent component is preferably a spray-dried granule or particle or powder.

When the component is in the form of an agglomerated granule, the cationic water-soluble compound is preferably combined with a carrier material.

The detergent component preferably forms part of a detergent composition.

5 The compositions in accordance with the invention can take a variety of physical forms including granular, tablet, flake, pastille and bar forms. The compositions are particularly the so-called concentrated granular detergent compositions adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

10

The components or compositions can also be used in or in combination with bleach additive compositions, for example comprising chlorine bleach.

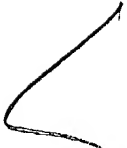
15 The mean particle size of the components of granular compositions in accordance with the invention, comprising the water-soluble cationic clay-soil removal/anti-redeposition compounds, should preferably be such that no more than 40% or preferably not more than 15% of the particles are greater than 1.8mm in diameter and not more than 40% or preferably not more than 15% of the particles are less than 0.25mm in diameter. Preferably the mean particle size is such that from 10%  
20 to 50% of the particles has a particle size of from 0.2mm to 0.7mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of sieves, preferably Tyler sieves. The weight fractions thereby obtained are plotted  
25 against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of granular detergent compositions typically is of at least 500 g/litre, more preferably from 600 g/litre to 1200 g/litre, preferably . When the  
30 detergent component is a spray-dried granule, particle or powder, a lower bulk density of the composition containing the component is preferred. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned  
35 cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower

extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

- 5 To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk  
10 density in g/litre. Replicate measurements are made as required.

- 15  Compacted solids may be manufactured using any suitable compacting process, such as tableting, briquetting or extrusion, preferably tableting. Preferably tablets for use in dish washing processes, are manufactured using a standard rotary tableting press using compression forces of from 5 to 13 KN/cm<sup>2</sup>, more preferably from 5 to 11KN/cm<sup>2</sup> so that the compacted solid has a minimum hardness of 176N to 275N, preferably from 195N to 245N, measured by a C100 hardness test as supplied by I. Holland instruments. This process may be used to prepare homogeneous or layered tablets of any size or shape. Preferably tablets are  
20 symmetrical to ensure the uniform dissolution of the tablet in the wash solution.

#### Laundry washing method

- 25 Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent component but preferably a composition comprising the component in accord with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as  
30 are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

- In a preferred use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to  
35 introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be

able to contain sufficient detergent product as would normally be used in the washing method.

5 The dispensing device containing the detergent product is placed inside the drum before the commencement of the wash, either before, or simultaneously with or after the washing machine has been loaded with laundry. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this  
10 product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively,  
15 the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

20 Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-  
25 2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly known as the "granulette". Another preferred dispensing device for use with the compositions of this invention is  
30 disclosed in PCT Patent Application No. WO94/11562.

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from  
35 a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the

washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially  
5 extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable  
10 protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent  
Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form  
15 of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

#### Machine dishwashing method

20 Any suitable methods for machine dishwashing or cleaning soiled tableware, particularly soiled silverware are envisaged.

A preferred machine dishwashing method comprises treating soiled articles selected  
25 from crockery, glassware, hollowware, silverware and cutlery and mixtures thereof, with an aqueous liquid having dissolved or dispensed therein an effective amount of a machine dishwashing component or preferably composition, comprising the component in accord with the invention. By an effective amount of the machine dishwashing composition it is meant from 8g to 60g of product  
30 dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

5		
	LAS	: Sodium linear C <sub>11-13</sub> alkyl benzene sulfonate
	TAS	: Sodium tallow alkyl sulfate
	CxyAS	: Sodium C <sub>1x</sub> - C <sub>1y</sub> alkyl sulfate
	C46SAS	: Sodium C <sub>14</sub> - C <sub>16</sub> secondary (2,3) alkyl sulfate
10	CxyEzS	: Sodium C <sub>1x</sub> -C <sub>1y</sub> alkyl sulfate condensed with z moles of ethylene oxide
	CxyEz	: C <sub>1x</sub> -C <sub>1y</sub> predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
	QAS	: R <sub>2</sub> .N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>12</sub> - C <sub>14</sub>
15	QAS 1	: R <sub>2</sub> .N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>8</sub> - C <sub>11</sub>
	QAS 2	: R <sub>2</sub> .N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>8</sub>
	APA	: C <sub>8</sub> - C <sub>10</sub> amido propyl dimethyl amine
	Soap	: Sodium linear alkyl carboxylate derived from an 0/20 mixture of tallow and coconut fatty acids
20	STS	: Sodium toluene sulphonate
	CFAA	: C <sub>12</sub> -C <sub>14</sub> (coco) alkyl N-methyl glucamide
	TFAA	: C <sub>16</sub> -C <sub>18</sub> alkyl N-methyl glucamide
	TPKFA	: C <sub>12</sub> -C <sub>14</sub> topped whole cut fatty acids
	STPP	: Anhydrous sodium tripolyphosphate
25	TSPP	: Tetrasodium pyrophosphate
	Zeolite A	: Hydrated sodium aluminosilicate of formula Na <sub>12</sub> (AlO <sub>2</sub> SiO <sub>2</sub> ) <sub>12</sub> .27H <sub>2</sub> O having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
30	NaSKS-6	: Crystalline layered silicate of formula δ- Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>
	Citric acid	: Anhydrous citric acid
	Borate	: Sodium borate
	Carbonate	: Anhydrous sodium carbonate with a particle size between 200μm and 900μm
35	Bicarbonate	: Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm

	Silicate	:	Amorphous sodium silicate ( $\text{SiO}_2:\text{Na}_2\text{O} = 2.0:1$ )
	Sulfate	:	Anhydrous sodium sulfate
	Mg sulfate	:	Anhydrous magnesium sulfate
	Citrate	:	Tri-sodium citrate dihydrate of activity 86.4%
5			with a particle size distribution between $425\mu\text{m}$ and $850\mu\text{m}$
	MA/AA 1	:	Copolymer of 3:7 maleic/acrylic acid, average molecular weight about 70,000
	MA/AA 2	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 3,000
10	MA/AA 3	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 12,000
	AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
15	CM	:	Sodium carboxymethyl cellulose
	Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
	Protease	:	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase
20	Protease I	:	Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
	Alcalase	:	Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
25	Cellulase	:	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
	Amylase	:	Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
30	Lipase	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase



	Lipase (1)	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
5	Endolase	:	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
	PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
	PB1	:	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
10	Percarbonate	:	Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
	NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt
	NAC-OBS	:	(6-nonamidocaproyl) oxybenzene sulfonate
15	TAED	:	Tetraacetylenediamine
	DTPA	:	Diethylene triamine pentaacetic acid
	DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
20	EDDS	:	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
	Photoactivated	:	Sulfonated zinc phthlocyanine encapsulated in bleach (1) dextrin soluble polymer
25	Photoactivated	:	Sulfonated alumino phthlocyanine encapsulated in bleach (2) dextrin soluble polymer
	Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
	Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate
	HEDP	:	1,1-hydroxyethane diphosphonic acid
30	PEGx	:	Polyethylene glycol, with a molecular weight of x (typically 4,000)
	PEO	:	Polyethylene oxide, with an average molecular weight of 50,000
	TEPAE	:	Tetraethylenepentaamine ethoxylate
35	PVI	:	Polyvinyl imidosole, with an average molecular weight of 20,000

	PVP	:	Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
	PVNO	:	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
5	PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
	QEA1	:	$\text{MeSO}_4^- \text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n) (\text{CH}_3) -\text{N}^+ - \text{C}_6\text{H}_{12} -\text{N}^+ - (\text{CH}_3) \text{bis}((\text{C}_2\text{H}_5\text{O})-(\text{C}_2\text{H}_4\text{O})_n)$ , wherein $n = \text{from } 20 \text{ to } 30$
10	QEA2	:	Salt of $\text{bis}((\text{C}_2\text{H}_5\text{O})-(\text{C}_2\text{H}_4\text{O})_n) (\text{CH}_3) \text{N}^+ \text{R}_1$ , wherein $\text{R}_1$ is $\text{C}_4\text{-C}_{12}$ alkyl group and $n = \text{from } 20 \text{ to } 30$
	QEA3	:	Salt of $\text{tri}\{(\text{bis}((\text{C}_2\text{H}_5\text{O})-(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3)-\text{N}^+)-(\text{CONC}_3\text{H}_6)\}-\text{C}_3\text{H}_6\text{O}$ , wherein $n = \text{from } 20 \text{ to } 26$
15	SRP 1	:	Anionically end capped poly esters
	SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
	PEI	:	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
20	Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
25	Opacifier	:	Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
	Wax	:	Paraffin wax

30

In the following examples all levels are quoted as % by weight of the composition:

**Example 1**

The following high density granular laundry detergent compositions A to F of particular utility under European machine wash conditions are examples in accord  
 5 with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
C46AS	1.0	2.0	2.5	-	3.0	4.0
C68AS	3.0	2.0	5.0	7.0	1.0	0.5
QAS	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	16.1	18.1	18.1	18.1
Zeolite MAP	-	4.0	3.5	-	-	-
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sodium Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
MA/AA 1	0.6	0.8	0.3	1.0	0.5	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5	1.0	1.5	-	1.5
Mn Catalyst	-	0.03	0.07	-	-	-
DTPMP	0.25	0.25	0.25	0.25	0.25	0.25

HEDP	0.3	0.3	0.2	0.2	0.3	0.3
EDDS	-	-	0.4	0.2	-	-
QEA 1	1.0	0.8	0.7	1.2	-	0.5
QEA 2	-	-	-	-	1.0	0.5
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.4	0.3	0.1	0.1
Photoactivate d bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

**Example 2**

The following high density granular laundry detergent compositions G to L of particular utility under European machine wash conditions are examples in accord with the invention:

	G	H	I	J	K	L
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
C46AS	1.0	2.0	2.5	-	3.0	4.0
C68AS	3.0	2.0	5.0	7.0	1.0	0.5
QAS	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	16.1	18.1	18.1	18.1
Zeolite MAP	-	4.0	3.5	-	-	-
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sodium Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
MA/AA 1	0.5	0.8	0.3	1.0	0.5	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5	1.0	1.5	-	1.5
Mn Catalyst	-	0.03	0.07	-	-	-
DTPMP	0.25	0.25	0.25	0.25	0.25	0.25

HEDP	0.3	0.3	0.2	0.2	0.3	0.3
EDDS	-	-	0.4	0.2	-	-
QEA 1	1.0	0.8	0.7	1.2	-	0.5
QEA 2	-	-	-	-	1.0	0.5
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.4	0.3	0.1	0.1
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

**Example 3**

The following granular laundry detergent compositions M to O of bulk density 750 g/litre are compositions according to the invention:

5

	M	N	O
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
QAS	0.8	2.0	-
QAS 1	0.4	1.0	2.5
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Citric acid	0.3	0.2	-

Silicate	6.8	-	-
Sodium sulfate	39.8	-	7.0
PB4	5.0	12.7	-
TAED	0.5	0.2	-
DPDA	-	-	0.3
NAC OBS	1.0	2.2	-
DTPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Protease	0.26	0.85	0.85
Lipase	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28
Amylase	0.1	0.1	0.1
MA/AA	0.5	0.8	0.4
QEA 1	1.0	1.5	-
QEA 2	-	-	0.8
CMC	0.2	0.4	0.4
PVP	-	-	0.8



Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04
Perfume	0.3	0.3	0.3
Silicone antifoam	0.5	2.4	2.4
Minors/misc to 100%	n.a.	n.a.	

**Example 4**

The following detergent formulations of particular utility under European machine wash conditions are examples in accord with the invention.

5

	P	Q	R	S
<b>Blown powder</b>				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	-	27.0	-	20.0
STPP	24.0	-	24.0	-
Sulfate	9.0	6.0	13.0	-
MA/AA 2	2.0	-	-	4.0
MA/AA 1	-	1.0	0.5	-
Silicate	7.0	3.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
QEA 1	0.8	1.0	3.0	0.5
QEA 2	-	-	-	0.5
Brightener	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	0.4	0.4	0.2	0.4
<b>Spray on</b>				
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.3	0.3	0.3	0.2
Silicone antifoam	0.3	0.3	0.3	-
<b>Dry additives</b>				
Sulfate	3.0	3.0	5.0	10.0
Carbonate	6.0	13.0	15.0	14.0
PB1	-	-	-	1.5
PB4	18.0	18.0	10.0	18.5
TAED	3.0	2.0	-	2.0
EDDS	-	2.0	2.4	-
Protease	1.0	1.0	1.0	1.0

Lipase	0.4	0.4	0.4	0.2
Amylase	0.2	0.2	0.2	0.4
Photoactivated bleach	-	-	-	0.15
Total	100.0	100.0	100.0	100.0

**Example 5**

The following detergent formulations of particular utility under European machine wash conditions are examples in accord with the invention.

	T	U	V	W
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	24.0	-	-	20.0
STPP	-	27.0	24.0	-
Sulfate	9.0	6.0	13.0	5.0
QAS 1	0.5	0.8	-	1.0
MA/AA 1	0.4	0.9	-	-
MA/AA2	-	-	0.4	0.5
QEA 1	1.0	1.2	0.7	-
QEA 3	-	-	-	0.5
Silicate	1.0	7.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
Carbonate	5.0	3.0	-	4.0
STS	0.3	0.5	-	0.2
DTPMP	0.4	0.4	0.2	0.4
Spray on				
Brightener	0.02	-	-	0.02
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.5	0.3	0.5	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
QEA	-	-	-	0.5
EDDS	0.3	-	-	-

Sulfate	2.0	3.0	5.0	10.0
Carbonate	6.0	10.0	12.0	9.0
Citric acid	2.5	-	-	2.0
QAS II	0.5	-	-	0.5
SKS-6	10.0	-	-	-
Percarbonate	18.5	-	-	-
PB4	-	18.0	10.0	21.5
TAED	2.0	2.0	-	2.0
NAC-OBS	3.0	2.0	4.0	-
Protease	1.0	1.0	1.0	1.0
Lipase	-	0.4	-	0.2
Lipase (1)	0.4	-	0.4	-
Amylase	0.2	0.2	0.2	0.4
Brightener 1	0.05	-	-	0.05
Misc/minor to 100%				

**Example 6**

The following granular detergent formulations are examples in accord with the invention.

5

	X	Y	Z	AA	BB	CC
Blown powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	0.4	-	-	0.3
MA/AA (1)	0.9	-	-	-	-	-
AA	-	-	0.1	1.0	-	0.2
QAS 1	0.5	0.6	-	-	1.0	1.0
Sulfate	5.0	6.3	14.3	11.0	15.0	15.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0
QEA 1	0.9	1.1	-	-	-	0.5
QEA 2	-	-	1.0	1.5	-	-
QEA 3	-	-	-	-	-	0.5
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
STS	0.2	-	-	0.5	0.3	0.2
DTPA	-	0.3	0.3	-	-	0.4
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray on						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0

QEA 1	-	-	-	-	0.8	-
MA/AA 1	-	-	-	-	0.8	-
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (water etc)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS (I)	-	-	-	-	1.0	-
Citric acid	-	0.4	-	-	2.0	0.5
PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6
Methyl cellulose	0.2	-	-	-	-	-
SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Cumene sulfonic acid	-	1.0	-	-	-	2.0
Lipase	0.2	-	0.2	-	0.2	0.4
Cellulase	0.2	0.2	0.2	0.3	0.2	0.2
Amylase	0.2	-	0.1	-	0.2	-
Protease	0.5	0.5	0.5	0.3	0.5	0.5
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP1	0.2	0.5	0.3	-	0.2	-
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-
Misc/minors to 100%						


**Example 7**

The following nil bleach-containing detergent formulations of particular use in the washing of coloured clothing, are examples according to the present invention were prepared:

5

	DD	EE	FF
<b>Blown Powder</b>			
Zeolite A	15.0	15.0	-
Sulfate	0.0	10.0	-
LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
QEA 1	1.0	0.2	-
QEA 2	-	1.0	-
MA/AA 1	0.5	-	-
AA	-	0.6	-
Carbonate	-	5.0	-
STS	-	0.2	-
QAS 1	-	1.0	-
<b>Agglomerates</b>			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
QEA 1	-	-	1.0
CMC	-	-	0.5
MA/AA	-	-	0.8
Carbonate	9.0	7.0	7.0
<b>Spray On</b>			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
<b>Dry additives</b>			





MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Citric Acid	-	1.0	-
Sulfate	0.0	9.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	700	700	700

**Example 8**

The following granular detergent compositions of particular utility under European wash conditions are examples in accord with the invention.

5

	EE	FF
Blown powder		
Zeolite A	20.0	-
STPP	-	20.0
LAS	6.0	6.0
C68AS	2.0	2.0
Silicate	3.0	8.0
MA/AA 1	4.0	2.0
MA/AA 2	-	2.0
CMC	0.6	0.6
QEA 1	0.9	0.6
QEA 3	0.1	-
Brightener 1	0.2	0.2
DTPMP	0.4	0.4
Spray on		
C45E7	5.0	5.0
Silicone antifoam	0.3	0.3
Perfume	0.2	0.2
Dry additives		
Carbonate	14.0	9.0
PB1	1.5	2.0
PB4	18.5	13.0
TAED	2.0	2.0
Photoactivated bleach	15 ppm	15 ppm
Protease	1.0	1.0
Lipase	0.2	0.2
Amylase	0.4	0.4
Cellulase	0.1	0.1
Sulfate	10.0	20.0

Balance (Moisture and Misc.)		
Density (g/litre)	700	700

**Example 9**

The following detergent compositions, are examples according to the present invention:

5

	GG	HH	II
<b>Blown Powder</b>			
Zeolite A	15.0	15.0	15.0
Sodium Sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	0.4
CMC	0.4	0.4	0.4
MA/AA 1	-	-	2.0
MA/AA 2	2.0	-	-
AA	-	4.0	-
<b>Agglomerates</b>			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
QEA 1	1.0	2.5	0.6
Mn Catalyst	0.03	-	-
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
<b>Spray On</b>			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
<b>Dry additives</b>			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
Percarbonate	-	7.0	10.0
TAED	6.0	2.0	5.0

PB1	14.0	7.0	10.0
EDDS	-	2.0	-
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Misc.)	100.0	100.0	100.0
Density (g/litre)	850	850	850

**Example 10**

The following granular detergent formulations are examples in accord with the invention.

5

	JJ	KK	LL	MM
Base granule				
Zeolite A	30.0	22.0	24.0	10.0
Sulfate	10.0	5.0	10.0	7.0
MA/AA 1	-	0.5	-	-
AA	0.9	-	1.0	-
MA/AA 2	-	-	-	1.0
QEA 1	-	1.2	1.2	-
QEA 3	1.5	-	-	3.0
QAS 2	-	1.0	0.5	-
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AES	-	1.0	1.0	-
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray on				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
Dry additives				
Carbonate	5.0	10.0	18.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	1.0	1.0	1.0	0.5
Lipase	0.4	-	-	0.4
Amylase	0.1	-	-	0.1

Cellulase	0.1	0.2	0.2	0.1
NOBS	-	4.0	-	4.5
PB1	1.0	5.0	1.5	6.0
Sulfate	4.0	5.0	-	5.0
SRPI	-	0.4	-	-
Sud supressor	-	0.5	0.5	-
Misc/minor to 100%				

**Example 11**

The following granular detergent compositions are examples in accord with the invention.

5

	NN	OO	PP	QQ	RR	SS	TT	UU
Blown powder								
Zeolite A	20.0	-	15.0	15.0	15.0	15.0	15.0	15.0
STPP	-	20.0	-	-	-	-	-	-
Sulphate	-	-	15.0	15.0	15.0	15.0	15.0	15.0
Carbonate	-	-	5.0	5.0	5.0	5.0	5.0	5.0
TAS	-	-	1.0	1.0	1.0	1.0	1.0	1.0
LAS	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Silicate	3.0	8.0	-	-	-	-	-	-
QEA 1	1.2	1.5	0.9	0.9	0.9	0.9	0.9	0.9
QAS 1	1.2	-	0.9	-	0.9	-	-	-
QAS	-	1.5	-	0.9	-	0.9	-	-
MA/AA 1	1.7	1.7	0.5	0.5	0.5	0.5	0.5	0.5
CMC	0.4	0.4	0.2	0.2	0.2	0.2	0.2	0.2
Brightener 1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1
DTPMP	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1
STS	-	1.0	1.0	1.0	-	-	1.0	-
Spray on								
C45E7	5.0	5.0	4.0	4.0	4.0	4.0	4.0	4.0
Silicone antifoam	0.3	0.3	0.1	0.1	0.1	0.1	0.1	0.1
Perfume	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3
Dry additives								
QEA	1.0	1.0	-	-	-	-	-	-
Carbonate	14.0	9.0	10.0	10.0	10.0	10.0	10.0	10.0
PB1	1.5	2.0	-	-	-	-	-	-
PB4	18.5	13.0	13.0	13.0	13.0	13.0	13.0	13.0
TAED	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
QAS 1	1.0	1.0	-	-	-	-	1.0	1.0
Photoactivated bleach	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm



SKS-6	-	-	3.0	3.0	3.0	3.0	3.0	3.0
Protease	1.0	1.0	0.2	0.2	0.2	0.2	0.2	0.2
Lipase	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Amylase	0.4	0.4	0.2	0.2	0.2	0.2	0.2	0.2
Cellulase	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2
Sulfate	10.0	20.0	5.0	5.0	5.0	5.0	5.0	5.0
Misc/minors to 100%								
Density (g/litre)	690	690	690	690	690	690	690	690

**Example 12**

The following laundry bar detergent compositions are examples in accord with the invention.

5

	VV	WW	XX	YY	ZZ	AB	AC	AD
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Sodium laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Calcium carbonate	21.5	-	-	-	-	-	-	-
Sulfate	5.0	-	-	-	-	-	-	-
TSPP	5.0	-	5.0	-	5.0	5.0	2.5	5.0
STPP	5.0	15.0	-	-	-	5.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DTPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
MA/AA 1	0.4	1.0	-	-	0.2	0.4	0.5	0.4
MA/AA 2	-	-	0.9	1.2	0.8	0.8	-	-
SRP1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Protease	-	0.12	-	0.08	0.08	-	-	0.1
Lipase	-	0.1	-	0.1	-	-	-	-
Amylase	-	-	0.8	-	-	-	0.1	-
Cellulase	-	0.15	-	-	0.15	-	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.6	-	-	-	-	-	-	-

**Example 13**

The following compact high density (0.96Kg/l) dishwashing detergent compositions NN to SS are examples in accord with the invention and the abbreviated component identifications, used in the dish washing detergent compositions, have the following meanings:

Metasilicate	:	Sodium metasilicate ( $\text{SiO}_2:\text{Na}_2\text{O}$ ratio = 1.0)
Nonionic	:	C <sub>13</sub> -C <sub>15</sub> mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by BASF GmbH (low foaming)
PAAC	:	Pentaamine acetate cobalt (III) salt
BzP	:	Benzoyl Peroxide
Paraffin	:	Paraffin oil sold under the tradename Winog 70 by Wintershall.
BTA	:	Benzotriazole
Bismuth nitrate	:	Bismuth nitrate salt
Terpolymer	:	Terpolymer of average molecular weight approx. 7,000, comprising acrylic: maleic: ethylacrylic acid monomer units at a weight ratio of 60:20:20
480N	:	Random copolymer of 3:7 acrylic/methacrylic acid, average molecular weight about 3,500

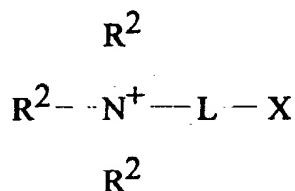
	AE	AF	AG	AH	AI	AJ
STPP	24.80	24.80	25.00	28.39	28.50	20.00
Citrate	-	-	-	-	10.00	10.00
Carbonate	-	-	17.50	17.50	-	-
QEA 1	0.5	1.5	2.0	1.0	1.3	0.8
Silicate	20.36	20.36	14.81	14.81	14.81	-
Metasilicate	2.50	2.50	2.50	-	-	-
PB1	7.79	7.79	9.74	14.28	9.74	-
PB4		-	-	-	-	10.4
Percarbonate	-	-	-	-	-	6.70
Non-ionic	1.50	1.50	2.00	1.50	2.00	2.60
TAED	2.39	2.00	2.70	2.00	3.60	4.00
HEDP	0.46	0.46	1.00	-	0.83	-
DETPMP	-	-	0.65	-	-	-
PAAC	-	-	-	0.20	-	-
BzP	-	-	-	4.44	-	-
Paraffin	0.50	0.50	0.50	0.50	-	0.20
Protease	2.20	2.20	2.20	2.20	2.00	0.50
Amylase	1.50	1.50	1.20	1.50	1.00	1.10
BTA	0.30	0.30	0.30	0.30	-	-
Bismuth Nitrate	-	-	0.30	-	-	-
Terpolymer	-	-	-	4.00	-	-
MA/AA 2	0.5	1.0	1.00	0.50	0.7	0.8
Sulphate	8.44	8.44	20.77	-	23.24	1.00
Misc inc moisture to balance						
pH (1% solution)	10.90	10.90	11.00	10.80	10.90	9.60

Claims

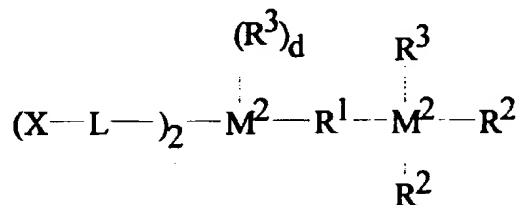
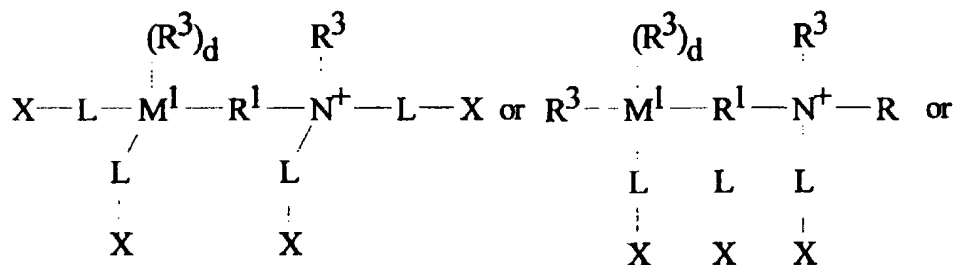
1. A solid, preferably granular detergent composition or component thereof comprising

- (a) a carboxylate-containing polyelectrolyte compound; and
- (b) a water-soluble cationic compound having clay soil removal/anti-redeposition properties, which is selected from the group consisting of:

- 1) ethoxylated cationic monoamines having the formula:

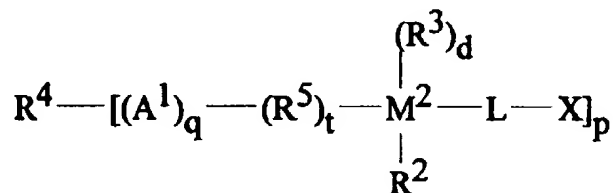


- 2) ethoxylated cationic diamines having the formula:



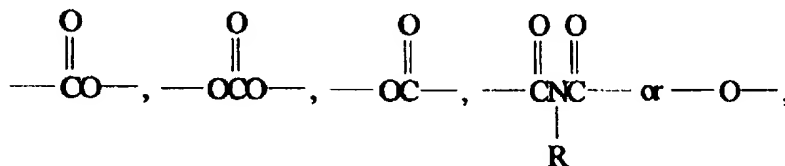
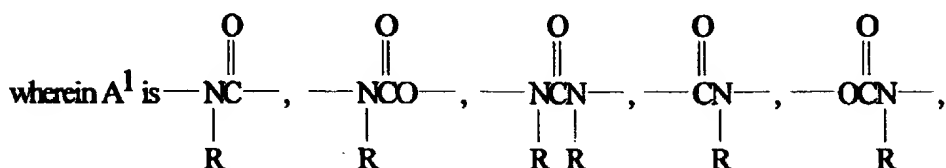
- wherein  $\text{M}^1$  is an N+ or N group; each  $\text{M}^2$  is an N+ or N group, and at least one  $\text{M}^2$  is an N+ group;

3) ethoxylated cationic polyamines having the formula:



5

4) mixtures thereof;



- 10 R is H or C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl, R<sup>1</sup> is C<sub>2</sub>-C<sub>12</sub> alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C<sub>2</sub>-C<sub>3</sub> oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R<sup>2</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl, the moiety -L-X, or two R<sup>2</sup> together form the moiety -(CH<sub>2</sub>)<sub>r</sub>-A<sup>2</sup>-(CH<sub>2</sub>)<sub>s</sub>, wherein A<sup>2</sup> is -O- or -CH<sub>2</sub>-, r is 1 or 2, s is 1 or 2
- 15 and r + s is 3 or 4; each R<sup>3</sup> is C<sub>1</sub>-C<sub>8</sub> alkyl or hydroxyalkyl, benzyl, the moiety L-X, or two R<sup>3</sup> or one R<sup>2</sup> and one R<sup>3</sup> together form the moiety -(CH<sub>2</sub>)<sub>r</sub>-A<sup>2</sup>-(CH<sub>2</sub>)<sub>s</sub>; R<sup>4</sup> is a substituted C<sub>3</sub>-C<sub>12</sub> alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl group having p substitution sites; R<sup>5</sup> is C<sub>1</sub>-C<sub>12</sub> alkenyl, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C<sub>2</sub>-C<sub>3</sub> oxyalkylene moiety having from 2 to
- 20 about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; X is a nonionic group selected from the group consisting of H, C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof; L is a hydrophilic chain which contains the polyoxyalkylene moiety

$-(R^6O)_m(CH_2CH_2O)_n-$ ; wherein  $R^6$  is  $C_3$ - $C_4$  alkylene or hydroxyalkylene and  $m$  and  $n$  are numbers such that the moiety

$-(CH_2CH_2O)_n-$  comprises at least about 50% by weight of said polyoxyalkylene moiety;  $d$  is 1 when  $M^2$  is  $N^+$  and is 0 when  $M^2$  is  $N$ ;  $n$  is at least about 16 for said cationic monoamines, is at least about 6 for said cationic diamines and is at least about 3 for said cationic polyamines;  $p$  is from 3 to 8;  $q$  is 1 or 0;  $t$  is 1 or 0, provided that  $t$  is 1 when  $q$  is 1.

and wherein the ratio of compound (a) to (b) is from 1:95 to 95:1.

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2. A detergent composition or component according to Claim 1 wherein said ratio is from 1:25 to 25:1.

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3. A detergent component according to Claim 1 wherein said ratio is from 1:1 to 1:10.

4. A detergent component according to Claim 1 or 3 wherein said ratio is from 1:1 to 1:2.

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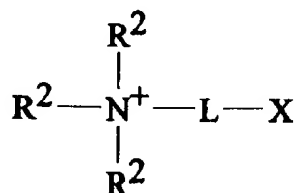
5. A detergent component which is a spray-dried particle comprising

(a) a carboxylate-containing polyelectrolyte compound; and

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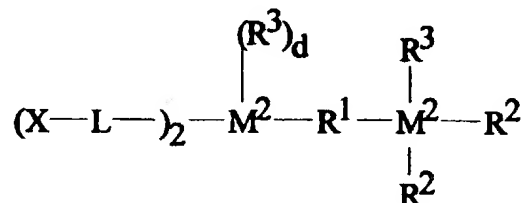
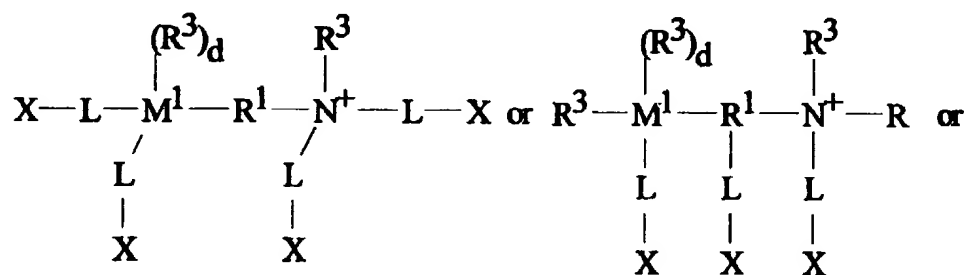
(b) a water-soluble cationic compound having clay soil removal/antiredeposition properties, which is selected from the group consisting of:

1) ethoxylated cationic monoamines having the formula:



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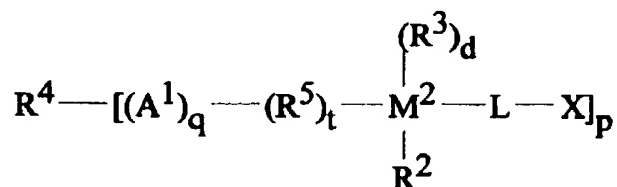
2) ethoxylated cationic diamines having the formula:



wherein  $\text{M}^1$  is an N+ or N group; each  $\text{M}^2$  is an N+ or N group, and at least one  $\text{M}^2$  is an N+ group;

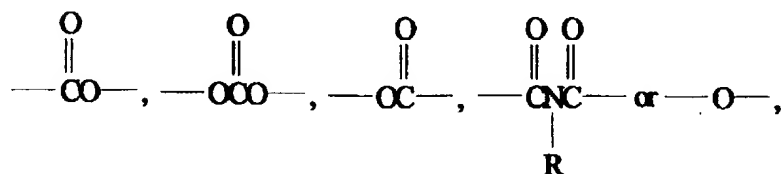
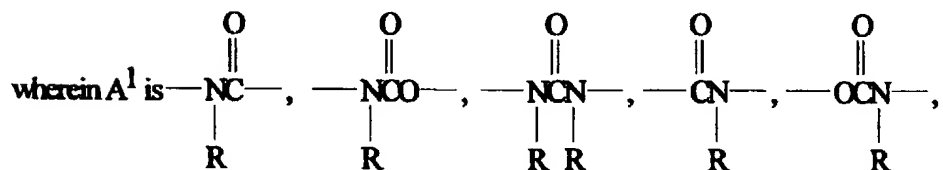
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3) ethoxylated cationic polyamines having the formula:



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4) mixtures thereof;





R is H or C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl, R<sup>1</sup> is C<sub>2</sub>-C<sub>12</sub> alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C<sub>2</sub>-C<sub>3</sub> oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R<sup>2</sup> is

5 C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl, the moiety -L-X, or two R<sup>2</sup> together form the moiety -(CH<sub>2</sub>)<sub>r</sub>-A<sup>2</sup>-(CH<sub>2</sub>)<sub>s</sub>-, wherein A<sup>2</sup> is -O- or -CH<sub>2</sub>-, r is 1 or 2, s is 1 or 2 and r + s is 3 or 4; each R<sup>3</sup> is C<sub>1</sub>-C<sub>8</sub> alkyl or hydroxyalkyl, benzyl, the moiety L-X, or two R<sup>3</sup> or one R<sup>2</sup> and one R<sup>3</sup> together form the moiety -(CH<sub>2</sub>)<sub>r</sub>-A<sup>2</sup>-(CH<sub>2</sub>)<sub>s</sub>-; R<sup>4</sup> is a substituted C<sub>3</sub>-C<sub>12</sub> alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl

10 group having p substitution sites; R<sup>5</sup> is C<sub>1</sub>-C<sub>12</sub> alkenyl, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C<sub>2</sub>-C<sub>3</sub> oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; X is a nonionic group selected from the group consisting of H, C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof; L is a hydrophilic chain

15 which contains the polyoxyalkylene moiety -(R<sup>6</sup>O)<sub>m</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>-; wherein R<sup>6</sup> is C<sub>3</sub>-C<sub>4</sub> alkylene or hydroxyalkylene and m and n are numbers such that the moiety -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>- comprises at least about 50% by weight of said polyoxyalkylene moiety; d is 1 when M<sup>2</sup> is N<sup>+</sup> and is 0 when M<sup>2</sup> is N; n is at least about 16 for

20 said cationic monoamines, is at least about 6 for said cationic diamines and is at least about 3 for said cationic polyamines; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1.

and wherein the ratio of compound (a) to (b) is from 1:1 to 1:10.

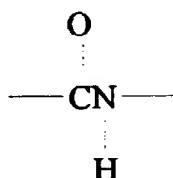
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6. A detergent component or component according to any preceding Claim wherein the cationic compound is present at a level of from 0.5% to 15% by weight of the component or particle.

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7. A detergent composition or component according to any preceding Claim wherein the cationic compound is present at a level of from 0.01% to 30% by weight of the composition.

8. A detergent composition or component according to any preceding Claim wherein the cationic compound is present at a level of from 0.2% to 3% by weight of the composition.
- 5 9. A detergent composition or component according to any preceding Claim wherein said cationic compound is an ethoxylated cationic monoamine and is characterised in that one  $R^2$  is methyl, two  $R^2$  are the moiety L-X, m is 0 and n is at least about 20.
- 10 10. A detergent composition or component according to any of the Claims 1 to 8 wherein said cationic compound is an ethoxylated cationic diamine and is characterised in that  $R^1$  is a  $C_2-C_6$  alkylene.
- 15 11. A detergent composition or component according to any of Claims 1 to 8 or 10 wherein said ethoxylated cationic diamine is characterised in that  $R^1$  is hexamethylene.
- 20 12. A detergent composition or component according to any of Claims 1 to 8 wherein said cationic compound is an ethoxylated cationic polyamine and is characterised in that  $R^4$  is a substituted  $C_3-C_6$  alkyl, hydroxyalkyl or aryl group;  $A_1$  is



25 and p is from 3 to 6.

13. A detergent composition or component according to any of Claims 10 to 12, wherein the cationic compounds is characterised in that each  $R^2$  is methyl or the moiety -L-X, each  $R^3$  is methyl and  $M^1$  and each  $M^2$  are an  $N^+$  group.
- 30 14. A detergent composition or component according to any of Claims 10 to 13 wherein m is 0 and n is at least 12.

15. A detergent composition or component according to Claims 10 or 11 wherein m is 0 and n is at least 20.
- 5 16. A detergent composition or component according to any of the preceding Claims, wherein the cationic water-soluble compound has one or more anionic counterions in the form of  $\text{MeSO}_4^-$ .
- 10 17. A detergent composition or component according to any preceding Claim wherein the carboxylate-containing polyelectrolyte compound is present at a level of from 0.01 % to 40% by weight of the composition.
- 15 18. A detergent component according to Claim 17 wherein the carboxylate-containing polyelectrolyte compound is present at a level of from 0.1 % to 15% by weight of the component.
- 20 19. A detergent component according to Claim 18 wherein the carboxylate-containing polyelectrolyte compound is present at a level of from 0.2% to 2.0%, preferably 1.2% by weight of the component or particle.
- 25 20. A detergent composition or component according to any of Claims 1 to 19 wherein the carboxylate-containing polyelectrolyte compound is a maleic/ acrylic co-polymer or acrylic homo-polymer.
- 30 21. A detergent composition or component according to Claim 20 wherein the maleic/ acrylic co-polymer with an average molecular weight of from 2500 to 20000 or 60000 to 70000.
22. A detergent composition or component according to any preceding Claim wherein a cationic mono- or bis- alkoxylated amine surfactant is present.
23. A detergent composition or component according to any preceding Claim, wherein a carbonate salt and a sulphate salt are present.
- 35 24. A process for making a detergent component according to any preceding Claim which is a spray-dried particle, the process comprising the steps of

a) formation of a mixture of the cationic compound and the carboxylate-containing polyelectrolyte in a ratio of from 1:95 to 95:1, preferably from 10:1 to 1:1 and optionally additional detergent ingredients;

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b) spray-drying the mixture of a).

25. A process for making a detergent component according to any preceding Claim which is a spray-dried particle, the process comprising the steps of

10

a) formation of a mixture of the cationic compound and the carboxylate-containing polyelectrolyte in a ratio of from 1:95 to 95:1, preferably from 10:1 to 1:1;

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b) addition of additional detergent ingredients to the mixture of step a) to form a second mixture;

c) spray-drying the second mixture b).

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26. A process according to Claim 25 wherein the additional detergent ingredients are organic components.

27. A process according to Claim 26 wherein the second mixture is added to further additional detergent ingredients prior to the spray-drying step.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/16705

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>																				
IPC(6) :C11D 1/62 US CL :510/299, 330, 350, 360, 443, 476, 504, 517 According to International Patent Classification (IPC) or to both national classification and IPC																				
<b>B. FIELDS SEARCHED</b>																				
Minimum documentation searched (classification systems followed by classification symbols) U.S. : 510/299, 330, 350, 360, 443, 476, 504, 517																				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS ONLINE search terms: quaternary, cationic, alkoxylate, ethoxylate, granu?																				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>																				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
X	US 4,664,848 A (OH et al.), 12 May 1987, abstract, column 5, line 36-column 6, line 65; column 33, lines 5-15; column 34, line 57-column 35, line 19; column 35, lines 48-55.	1-5																		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																				
<table border="0"> <tr> <td>* Special categories of cited documents:</td> <td>*T</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>*A* document defining the general state of the art which is not considered to be of particular relevance</td> <td>*X</td> <td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>*B* earlier document published on or after the international filing date</td> <td>*Y</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>*A*</td> <td>document member of the same patent family</td> </tr> <tr> <td>*O* document referring to an oral disclosure, use, exhibition or other means</td> <td></td> <td></td> </tr> <tr> <td>*P* document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	*A* document defining the general state of the art which is not considered to be of particular relevance	*X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	*B* earlier document published on or after the international filing date	*Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family	*O* document referring to an oral disclosure, use, exhibition or other means			*P* document published prior to the international filing date but later than the priority date claimed		
* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																		
*A* document defining the general state of the art which is not considered to be of particular relevance	*X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																		
*B* earlier document published on or after the international filing date	*Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																		
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family																		
*O* document referring to an oral disclosure, use, exhibition or other means																				
*P* document published prior to the international filing date but later than the priority date claimed																				
Date of the actual completion of the international search 24 NOVEMBER 1997		Date of mailing of the international search report 21 JAN 1998																		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer JOHN R. HARDEE <i>John R. Hardee</i> Telephone No. (703) 308-0661																		

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/16705

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 6-27  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
1-5

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.